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Mercury in the Environment. A Compilation of Papers on the Abundance, Distribution, & Testing of Mercury in Rocks, Soils, Waters, Plants, and the Atmosphere

Geological Survey, Washington, D C

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Mercury in the Environment

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FOREWORD

Current interest in the distribution of mercury in the natural environment stems from two related concerns:

1. Mercury is an essential metal for industry, the known domestic resources of mercury ores are limited, and better knowledge of the geologic distribution and geochemistry of the element is needed to identify new reserves.
2. With the developing interest in environmental protection has come an increase in awareness of and concern for the actual and potential hazards of mercury wastes in the environment.

Abnormal quantities of mercury in fish and other foods have recently raised many questions about its natural occurrence and behavior. Like all other elements, this unusual metal has been part of our environment for all time.

The Geological Survey has devoted much effort to the study of mercury as part of its basic mission of determining the occurrence and distribution of mineral resources. This report discusses known facts about mercury—where, and in what forms and quantities mercury is found; how it behaves in air, water, and earth materials; the impact of man's activities on its distribution; and the effects of the element on our lives. Furthermore, mercury is a strategic metal and because the United States has traditionally relied on imports for approximately half of its requirements, there is obvious need for better understanding of the occurrence and distribution of mercury in this country. This report is written with the hope that the information will provide better understanding of the mercury problems which confront us.

W. T. Pecora
Director, U.S. Geological Survey

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MERCURY IN THE ENVIRONMENT

SUMMARY

Mercury, commonly called quicksilver, is one of the elements that make up the planet earth. In its elemental state at the earth's surface it is a silvery liquid metal, approximately 13½ times as heavy as water, and it is the only metal which occurs in liquid form at ordinary earth surface temperatures. Like other liquids, it vaporizes and condenses in a pattern determined by its own vapor pressure and by the temperature and barometric pressure of the environment in which it exists. It is absorbed and held tightly by a variety of materials such as plant fibers and soils. Like other metallic elements, it reacts with a great variety of inorganic and organic compounds to form simple and complex molecules ranging from cinnabar, a mercury sulfide and the most common ore mineral, to the metallo-organic complexes which have received recent world wide attention as potential water pollutants and biologic toxins.

The compounds of mercury, like many other chemical compounds, are dispersed throughout rocks, soil, air, water, and living organisms by a complex system of physical, chemical, and biological controls. Particular combinations of these controls have developed interesting patterns of mercury and its compounds in the world around us.

MINERALS AND ROCKS

Although there are more than a dozen mercury-bearing minerals, only a few occur abundantly in nature. Cinnabar, the sulfide, is the most important and contains 86 percent mercury by weight; it is usually formed geologically at low temperatures (less than 300°C). It is generally found in mineral veins or fractures, as impregnations, or having replaced quartz, in rocks near recent volcanic or hot-spring areas.

Mercury content of broad categories of rocks in the earth's crust range from 10 to 20,000 ppb[1] (parts per billion); 1 ppb is equivalent to 1 pound of mercury per billion pounds of rock. Less than 20 percent of recorded rock samples have more than 1,000 ppb. Igneous rocks—those formed by melting and cooling—are the basic sources of mercury. These generally contain less than 200 ppb of mercury and average 100 ppb. The mercury content of soils averages about 100 ppb and varies within relatively narrow limits. Sedimentary rocks resulting from weathering and deposited by physical, chemical, and biological processes also generally average less than 100 ppb of mercury and seldom exceed 200 ppb except for certain organic-rich shales which may reach concentrations of 10,000 ppb or more.

In addition to organic-rich shales, other rocks with abnormally high mercury contents are known to exist. The Donets Basin, Kerch-Taman area, and the Crimea of the Union of Soviet Socialist Republics where both igneous rocks and sedimentary rocks commonly contain 100 times the normal maximum (up to 20,000 ppb), probably are the best examples, but similar anomalies can be found elsewhere. For example, Green River shale samples of the western Colorado Plateau have yielded mercury values as high as 10,000 ppb.

Background concentrations of soils in California are 20 to 40 ppb. The Franciscan Formation of California, in which most of the state's mercury mines are located, has background values of 100 to 200 ppb; anomalies in soils around these mercury deposits are in the range of 10,000 to 100,000 ppb.

ATMOSPHERE

Because of mercury's tendency to vaporize, the atmosphere measured at ground level near mercury ore deposits may contain as much as 20,000 ng/m³ (nanograms per cubic meter) of mercury in air. One nanogram is one billionth (1/1,000,000,000) of a gram, or 0.035/1,000,000,000 of an ounce, and 1 cubic meter equals about 1¼ cubic yards. Expressed on a weight basis rather than on a volume basis (for comparison with contents of rocks) 20,000 ng/m³ represents almost 16 pounds of mercury per billion pounds of air. Because of similarities in the mineral systems, the next highest near-ground levels of atmospheric mercury occur over precious metal ores (up to 1,500 ng/m³) and copper ores (20 ng/m³) in that order.

[1] See end of "Summary" for discussion of units used in this report.

Whatever the source of natural atmospheric mercury, its pattern responds to meteorological controls and other natural laws. Thus, the maximum amount of mercury in air is found at about midday with much smaller amounts found in the morning and in the evening. In both cases, vapor density, like the density of the atmosphere, is greatest near the surface of the land and diminishes with altitude. For example, a concentration of 30,000 ng/m³ of mercury at ground level near a mercury mine was observed to diminish to only about 100 ng/m³ at 100 feet altitude, and a ground-level concentration of 600 ng/m³ at noon has been observed to drop to only 20 ng/m³ at 2:00 a.m.

RAIN

Rain washes mercury from the atmosphere just as it does certain other atmospheric components. Even near mercury ore deposits, tests have shown the mercury content of the atmosphere to be essentially zero immediately after a rainstorm. Such scrubbing accounts for the fact that the mercury content of rainwater averages about 0.2 ppb. Tests in Sweden have shown that mercury carried down by rain adds to each acre of land per year about the same amount of mercury one would expect to be added by mercury-bearing seed dressing for fungal control of cereal crops. Mercury from either source is held tightly by the upper 2 inches or so of soil.

SURFACE WATER, GROUND WATER, AND SEDIMENTS

Contact of water with soil and rock during storm runoff, percolation into the ground, and movements under the ground where different geochemical stresses prevail, results in a natural distribution of mercury in water. The pattern of such distribution depends on the dispersion of mercury in the earth's crust and a great variety of earth processes already mentioned. Surface waters, except where they are influenced by special geologic conditions, or more recently by manmade pollution, generally contain less than 0.1 ppb of mercury. This reflects the relatively low concentration of mercury in rainwater and the relatively tight bonding of mercury in organic and inorganic materials over which the water passes in its travel through the environment. A recent reconnaissance of river waters in 31 states showed that (1) 65 percent of the samples tested had mercury contents below 0.1 ppb, (2) 15 percent exceeded 1.0 ppb, and (3) only 5 percent were more than 5.0 ppb—the maximum considered safe for drinking water.

Higher concentrations of mercury are likely to occur in underground waters because of the longer and more intimate contact with mineral grains and other environmental factors. Limited sampling of oil-field brines in California showed them to contain from 100 to 200 ppb of mercury. Hot springs in the same state appear to range from 0.5 to 5.0 ppb, and one measurement as high as 20 ppb of mercury has been recorded for such water. Vapors issuing from fumaroles and steam condensing from hot springs also have relatively high mercury contents—as much as 6 ppb and 180 ppb, respectively. Fine-grained muds from pots and mud volcanoes in Yellowstone National Park yield mercury contents up to 150,000 ppb and measurements as high as 500,000 ppb have been made on enriched sediments from springs and pools in Yellowstone. Thermal waters of this kind have probably formed mercury ore deposits in the past. Some 5,500 tons of the metal have been mined from deposits around Sulphur Bank Spring in California.

Because of mercury's tendency to sorb readily on a variety of earth materials, particulate matter suspended in water and bottom sediments of streams are more likely to contain high concentrations of mercury than the water itself, whatever the source may be. The best estimate is that suspended matter may contain from five to 25 times as much mercury as the water around it in areas of industrial pollution. Sediments immediately downstream of mercury ore deposits and mercury-contaminated industrial discharges may contain from a few hundred to as much as several hundred thousand parts per billion of mercury.

Persistence and movement of mercury in surface streams also must be considered in evaluating environmental effects. Although a normal stream water of pH 5 to 9 saturated with mercury should contain about 25 ppb, the concentration downstream from a mercury source is likely to be much lower because of dilution, vaporization, precipitation, sorption and chemical reaction. For example, the mercury concentration in river water near a mercury anomaly was found to decrease from 135 ppb to 0.01 ppb in 30 miles of travel, and sediment in a Wisconsin river near a source of industrial pollution had a mercury content of more than 500,000 ppb, whereas sediment 20 miles downstream from the source of pollution had a content of only 400 ppb. The tendency of mercury to sink rapidly and combine with sulfide in anaerobic bottom sediments to form cinnabar, which is slightly soluble, appears to be a major scavenging mechanism. Another mechanism which keeps content of dissolved mercury low is the relatively high reactivity of mercury with organic sub-

stances and the resulting uptake by living and nonliving organic matter.

Because they serve as sediment traps and habitats for aquatic organisms, lakes and ponds are likely to serve as traps for mercury which enters them. The significance of such accumulations depends upon the solubility of the final mercury form in the particular environment.

PLANTS AND ANIMALS

Inorganic chemicals in soil and water are basic substances for living things. In an aquatic environment, such inorganics generally are utilized by low forms of life which in turn serve as steps in the food chain for higher forms of life up the ladder to the vertebrate species, including man. Although mercury is not known to be an essential part of the food chain, it is assimilated by organisms living in environments which contain it. This process is thought to be enhanced through conversion of inorganic mercury by certain anerobes to methyl mercury, a more soluble form. However, there still is no proof that proper energy gradients exist to promote such reactions. Mercury tends to concentrate in living tissue once it has been assimilated, and there is some evidence that the extent of concentration increases with each step up the food chain, from plankton to fish to man. If the supply is cut off, the organism tends to purge itself of mercury, but the efficiency of recovery varies from organ to organ and organism to organism. One study of fish after 10 days of exposure to water with nonlethal concentrations of ethyl mercury showed mercury concentrations ranging from 1,000 ppb in muscle tissue to 22,800 ppb in the blood; almost complete elimination of mercury occurred within 40 days, except for that in the liver and kidneys. Similar studies have shown concentration factors of 250 to 5,000 in algae, 1,000 to 10,000 in ocean fish, and as much as 100,000 in other forms of sea life. Birds which feed on fish combine high intake with high concentration factors to yield extreme body residues. The eagle owl is a prime example with mercury contents as high as 40,000 ppb in its feathers.

There is evidence also that each step in the food chain has a certain threshold for mercury above which permanent harm to the organism may occur. In some cases, toxicity apparently is catalyzed by synergistic effects of other heavy metals, such as copper, chromium, zinc and nickel. Critical levels of mercury in lower organisms, such as plankton, generally are thought to be in the range of 5 to 200 ppb, although some kinds of kelp appear to have tolerance as high as 60,000 ppb. The tolerance of fish is in the range of 20 to 9,000 ppb, depending on the particular species of fish and mercury compound. Human tolerance has not been thoroughly investigated, but is suspected to be comparatively low.

Terrestrial plants, like aquatic organisms, absorb minor elements, including mercury, from the soils in which they grow at rates depending on the quality of the environment and the genetic characteristics of the plants. Unlike aquatic organisms, there seems to be little tendency for terrestrial plants to concentrate mercury above environmental levels. Typical soils contain from 50 to 500 ppb of mercury (average about 100 ppb) and most of the plants which grow in them are likely to contain less than 500 ppb. When soil concentrations of mercury are extremely high—say 10,000 ppb or more in the vicinity of cinnabar deposits—plants growing in them actually are likely to have mercury contents far below the level of their environment; for example 1,000 to 3,500 ppb. Even in these instances, it is primarily the plants which are rooted through the surface soil into the mercury ore which have high mercury contents; shallower rooted plants are likely to show much lower levels.

A few plants apparently have unusual capacity to concentrate mercury and even to separate it in metallic form. Droplets of pure mercury have been found in seed capsules of members of the chickweed family and similar droplets of mercury occur under moss covers of forest floors near mercury deposits. In plants, as in animals, mercury tends to concentrate in fatty parts so that vegetable fats are relatively rich in mercury whenever the metal is present in the organic.

Toxicity of mercury to terrestrial plants apparently depends more on the chemical state of the element than on its concentration. Roses are so sensitive to elemental mercury that florists have learned by experience to avoid mercury thermometers in greenhouses for fear of breaking them and poisoning the plants. On the other hand, the same roses can be sprayed with organic mercury fungicide with little or no ill effects.

FOSSIL FUELS

Throughout eons of time, the products and residues of geochemical processes and the life cycles of terrestrial and aquatic organisms have combined to yield very appreciable mercury contents and distinct regional patterns in fossil fuel deposits upon which the world depends for much of its energy. Typical samples of bituminous coal from the United

States contain from 1 to 25 ppb of mercury and many anthracite coals contain from 1,300 to 2,700 ppb. Concentrations in crude petroleum and related tarry residues are even higher. Samples from California crudes yield mercury values in the range of 1,000 to 21,000 ppb; related tars which have lost much of their volatile hydrocarbons are known to contain as much as 500,000 ppb.

ISOTOPES

The unique properties of mercury account not only for its unusual pattern and behavior in nature, but make it an attractive metal for a variety of scientific and industrial uses. It is estimated that the United States alone uses more than about 3,500 tons of mercury per year—about 20 percent of the world's total annual production. Current annual production in the United States is about 1,000 metric tons per year primarily from mines in seven or eight western states although it occurs as a minor constituent in other ores mined and processed in many states. During the past 10 years, the United States has imported more than half the mercury used. Losses to the environment of mercury and mercury compounds from industrial processes in this country are estimated at 800 tons per year and superimpose a significant amount of manmade pollution upon the pattern established by nature. Bactericides flowing down the sinks of hospitals, pesticides and fungicides leaching or eroding from agricultural land, and waste effluents from caustic-chlorine plants and other industries add waste mercury to the water and the air—often as point sources of pollution which are particularly troublesome. Recent studies of an Interior Department task force revealed mercury contents of many industrial outfalls and sludge banks to range from a trace to 100,000 ppb. Several spectacular instances of human poisoning have been reported in recent years from consumption of fish exposed to local concentrations of mercury. The death of about 50 people from eating mercury-tainted fish from Minamata Bay, Japan, is the most renowned example (Minamata disease). The source of the mercury was reported to be methyl mercury in liquid outfall from a plastic manufacturing plant. Such cases of industrial contamination have led to intensified effort to develop better methods of detecting mercury; better systems for assessing its pattern in the environment; better understanding of its behavior, including its effects on human beings; better legislation for whatever control appears to be desirable and practicable.

DETECTION

Although simple prospecting methods have been available for a long time, advanced analytical methodology and precision needed to detect the very small concentrations now thought to be significant to human health have been available for only the past few years. The Geological Survey's analytical methods have progressed from improved wet chemical dithizone colorimetric method, through a series of spectrographic, atomic absorption, and activation analyses procedures, until it now is capable of measuring with confidence mercury concentrations as low as 1 part per trillion in the atmosphere and 0.1 ppb in water or earth materials. Reduced to its simplest description, the atomic absorption procedure, which presently is preferred for water analysis, consists of vaporizing the mercury into the beam of an ultraviolet lamp and analyzing the light pattern which results from this spectral screening process. Activation analysis consists of bombarding the sample with neutrons in an atomic reactor to create a radioactive isotope of mercury which reads out a characteristic fingerprint of photon radiation as it undergoes decay.

RECOVERY AND CLEANUP

Improved analytical and surveillance techniques and intense research on behavior of mercury are making it possible for industries to recover and conserve valuable mercury which might otherwise have escaped as waste and for environmental managers to accurately monitor that which does escape. Process improvement, waste water recycle, and a variety of byproduct recovery schemes have made it possible for many industries to trim mercury losses from hundreds of pounds per day to 1 pound per day or less. With growing awareness of the dangers of mercury pollution and increasing vigilance of our environmental monitoring, one can look to the future with considerably more optimism than was possible a year ago.

UNITS AND NOTATION

Throughout this publication, consistent units have been used as follows:

ppb (parts per billion): 1 ppb—1 pound of substance in a total of a billion pounds of material—in this case, 1 pound of mercury per billion pounds of solid or water.

ppm (parts per million): 1 ppm—1 pound of substance in a total of a million pounds of material—in this case, 1 pound of mercury per million pounds of solid or water; 1 ppm = 1,000 ppb.

µg/l (micrograms per liter). Equivalent to *parts per billion* in dilute solution such as relatively pure water.

mg/l (milligrams per liter). Equivalent to *parts per million* in dilute solutions such as relatively pure water. 1 mg/l = 1,000 µg/l = 1 ppm = 1,000 ppb.

ng/m³ (nanogram per cubic meter (of air)). Generally used for concentration in the atmosphere. 1 ng/m³ = 1,000 ppb.

> greater than.

< less than.

≈ approximately.

SUMMARY OF THE LITERATURE ON THE INORGANIC GEOCHEMISTRY OF MERCURY

By MICHAEL FLEISCHER

SUMMARY

The mercury content of most igneous rocks is generally less than 200 ppb and probably averages less than 100 ppb, except for alkalic igneous rocks and deep-seated eclogites and kimberlites that average several hundred parts per billion Hg. Rocks from a few areas in the world, notably Crimea and the Donets Basin, U.S.S.R., show extremely high contents of mercury, which makes general averages of abundance of doubtful significance.

Most sedimentary rocks have mercury contents less than 200 ppb Hg, except for shales, clays, and soils, for which the data show considerable variation with average contents of a few hundred parts per billion Hg. Shales rich in organic matter are notably enriched in mercury, suggesting that some of the mercury may be present as organic complexes. The data show very high contents of mercury in a few areas of the world, including those in which the igneous rocks have high contents. Most of the analyses of coals are from the Donets Basin, U.S.S.R., which again have high contents of mercury; a few scattered analyses from other areas make it plausible to assume the presence of low concentrations of mercury in most coals. Mercury has been reported in large amounts in petroleum from one host in California.

Most natural waters (ground water, river water, sea water) contain less than 2 ppb Hg. High concentrations of mercury have been found in waters from hot springs and in brines from a petroleum field in California. Mercury is presumably dissolved by ground waters passing over rocks and is added to waters in considerable amounts by industrial wastes, notably by alkali-chlorine plants using the mercury cell method and by the paper pulp industry. The mercury is apparently removed in large part by adsorption on clays and on hydrous oxides of iron and manganese, and also by algae and plankton.

Mercury is present in the atmosphere, with background values of less than 1 to a few nanograms (10^{-9} g) per cubic meter. Over metallic ore deposits, the content of mercury is appreciably higher. Volcanic emanations including those of mud volcano type, have high contents of mercury, and must contribute a large amount of mercury to the atmosphere. In addition to such "natural pollution," one must assume that mercury is added to the atmosphere by the burning of coal and petroleum and very likely from stack gases of smelters treating copper, lead, and zinc ores. No data are available on the amounts added by "man-made pollution" or on the time of residence in the atmosphere of mercury from "natural" or "man-made" pollution.

GENERAL GEOCHEMICAL CHARACTERISTICS OF MERCURY

Mercury has the atomic number 80 and atomic weight 200.59. It has seven stable isotopes with percent abundances 196, 0.15; 198, 10.1; 199, 17.0; 200, 23.3; 201, 13.2; 202, 29.6; and 204, 6.7. Mercury is generally classed as a chalcophilic element, that is, one that tends to concentrate in sulfides. There are many minerals of mercury; the commonest are the sulfides cinnabar and metacinnabar and native mercury. Mercury is commonly present in tetrahedrite (up to 17.8 percent in the variety schwatzite), in sphalerite (up to 1 percent), and in wurtzite (up to 0.3 percent); it is present in small amounts in many other sulfides and sulfosalts. The element's unusually high volatility accounts for its presence in the atmosphere in appreciable amounts. Its ionic radius (Hg^{++}) is generally given as 1.06–1.12 angstroms, so that in the lithosphere it might be expected to accompany Ba, Sr, and Ca; this probably accounts for the high amounts of mercury found in some barites, celestites, and in alkalic igneous rocks.

ABUNDANCE AND DISTRIBUTION OF MERCURY

Nearly all the data available have been obtained during the past 30 years and most of it, during the past 10 years. As apparent from the summary that follows, the information available is inadequate to give a clear picture of the geochemical cycle of mercury or even to make accurate estimates of its abundance in common rock types.

This is in large measure due to the difficulty of analyzing rocks, soils, waters, and air for the very small amounts of mercury present, generally in parts per billion or parts per million.

Many methods have been used for the determination of these small amounts of mercury. Among them are the spectrographic method (usually with a sensitivity of 100 ppb, and extended to 10 ppb in improved procedures), separation of mercury by distillation followed by determination by measurement of the collected mercury globule or by a colorimetric method (the latter used in most of the analyses in the U.S.S.R.), separation by extraction and colorimetric determination, neutron activation analysis, and atomic absorption spectrophotometry.

Comparative data on precision and accuracy are available only for the last two methods. (See table 1.[1]) Comparison of the data published by many investigators indicates that the methods give results comparable to better than a factor of 5 and, hence, the averages are within an order of magnitude of the true values.

An even greater difficulty is that of weighting the results available. It is now well established that ore deposits of heavy metals such as copper, lead, and zinc, are surrounded by aureoles in which notable enrichment in mercury has occurred; this is now a recognized method of prospecting for ore deposits. (See, for example, Friedrich and Hawkes (1966), James (1962), Ozerova (1962), Saukov (1946), and Warren and others (1968).) As a result, it is necessary to discriminate between normal samples and those from mineralized areas.

A further problem is that the data show very clearly that some areas in the world (notably the Donets Basin, Kerch-Taman area, and Crimea, U.S.S.R.) show extremely high mercury contents in nearly all the rocks analyzed (100 times normal contents or more). The reasons for this are not yet known and it is not known how many such areas there may be.

[1] Tables are in the back of the report.

MERCURY IN IGNEOUS ROCKS

Analyses of basalts, gabbros, diabases, andesites, dacites, and rhyolitic rocks are given in table 2; analyses of granitic rocks are given in table 3. Most of them show contents of less than 200 ppb Hg and the average content is probably less than 100 ppb. The two recent analyses of ultramafic rocks in table 4 show less than 10 ppb Hg. The data show no clear-cut differences between the mafic and the silicic igneous rocks, although there is a slight suggestion that the silicic rocks have somewhat higher contents.

Two types of igneous rocks—deep-seated eclogites and kimberlites (table 4) and the alkalic rocks (table 5)—shows markedly higher contents of mercury, with averages of several hundred parts per billion Hg. Analyses of the individual minerals of alkalic rocks show fairly uniform distribution of mercury in the main rock-forming minerals, and high concentrations in some of the accessory minerals of high calcium, strontium, and barium contents (sphene, aegirine, lamprophyllite). Similar studies have not been made of the individual minerals of eclogites or kimberlites.

The foregoing picture is greatly complicated by the fact that analyses of all types of rocks from certain areas (notably in Crimea and the Donets Basin) show extremely high contents of mercury (up to 100 times as much as those of tables 3 and 5). These analyses have therefore been separated in table 6. It is possible that these high values represent analytical error, but this seems unlikely because one of the laboratories reporting them has also reported low "normal" values for similar rocks from other areas (table 3). The two areas have some mercury mineralization; they also are near areas of mud volcanoes that could have been sources of considerable amounts of mercury. (See "Mercury in sedimentary rocks and soils.") It should be noted that basaltic and andesitic lavas from Kamchatka and the Kurile Islands (table 2) have somewhat higher than average contents of mercury. These are, however, far less than many of the contents reported in table 6, even though the volcanic activity of this area also contributes considerable amounts of mercury.

MERCURY IN METAMORPHIC ROCKS

The few analyses available of mercury in metamorphic rocks (table 7) show the same wide variation as the analyses of sedimentary rocks. (See "Mercury in sedimentary rocks and soils.") Two series of analyses (Ozerova and Aidin'yan, 1966a, 1966b) showed little variation of mercury content

with grade of metamorphism; this was contrary to the expectation that high-grade metamorphism would cause mercury to be driven out of the rocks.

MERCURY IN SEDIMENTARY ROCKS AND SOILS

Analyses are collected of limestones (table 8), sandstones (table 9), shales and clays (table 10), miscellaneous sediments (table 11), oceanic and lacustrine sediments (table 12), and soils (table 13).

Except for the areas that showed high contents in igneous rocks, nearly all analyses of limestones and sandstones gave less than 200 ppb Hg, with averages perhaps of 30 to 50 ppb Hg. The analyses from the Donets Basin and Crimea show much higher contents of mercury (up to 100 times).

Considerable variation is shown by the analyses of shales and clays; again samples from Crimea, the Donets Basin, and the Kerch Peninsula are anomalously high. It has been suggested that these rocks might have been enriched in mercury by accumulation of the exhalations of mud volcanoes (tables 10, 11, 13, 15). The data of table 11 and table 12 suggest that mercury is enriched in sedimentary Fe and Mn ores, perhaps by adsorption or coprecipitation. Bituminous shales are notably richer in mercury than other shales, suggesting the possibility that mercury may be present as some form of organic complex.

The analyses of soils in table 13 are similar in general range to those of shales and clays. High values in soils above mineralized zones have been reported by many investigators. It has been suggested that the widespread use of organic mercury compounds as seed fungicides has increased the content of mercury in cultivated soils, but no data on this have been found.

MERCURY IN COAL AND PETROLEUM

The data on coals (table 16) are unrepresentative. Stock and Cucuel (1934a) found 1.2 to 25 ppb Hg (average, 12 ppb) in 11 coals. Brandenstein, Janda, and Schroll (1960) found 1,200 and 3,700 ppb Hg in two anthracites; the remaining 117 samples contained less than 1,000 ppb Hg. Headlee and Hunter (1953) reported <100,000 to 300,000 ppb Hg (average, 120,000 ppb) in the ashes of coals from West Virginia (each content not given). About 1,000 samples from the Donets Basin, U.S.S.R., have been analyzed (Dvornikov, 1963, 1965, 1967a, 1967b, 1968; Bol'shakov, 1961; Karasik, Vasilev'skaya, Petrov, and Ratenkhin, 1962; Ozerova, 1962; and Thach, 1966). This is an area with high contents of mercury in all the igneous and sedimentary rocks and in which commercial mercury ores occur closely associated with coals. Background values for coals not closely associated with mineralization are variously stated by these authors as 200, 400, and 700 ppb Hg, but very much higher values (up to 500,000 ppb) have been reported from coal in leases in mercury deposits. Analyses show that the mercury is mostly concentrated in iron sulfides in the coal deposits; the mercury is generally considered to be epigenetic and not syngenetic in origin. However, Shcherbakov, Dvornikov, and Zakrevich'naya (1970) found that much of the mercury in these coals is present as organic compounds and suggest that the mercury is syngenetic.

The only analyses of petroleum for mercury are those of Bailey, Snavely, and White (1961), who found 1,000 to 2,000 ppb Hg in petroleum from the Cymric field, California.

MERCURY IN NATURAL WATERS

The available data on mercury in natural waters are given in table 14. Most contain tenths of a part per billion to a few parts per billion. Insufficient data are given to permit assessment of the contribution of contamination. The mercury content of Atlantic Ocean waters is stated to increase with the amount of suspended material. The suspended matter of three samples of river waters contained 0.08 to 0.2 percent Hg, according to Kvashnevskaya and Shabkovskaya (1963), but the proportions of mercury in solution and in suspension are not stated. The high contents recorded for brines associated with a petroleum field and in a geothermal well are noteworthy. Data on some hot springs associated with volcanism are discussed later.

According to Aidin'yan and Belavskaya (1963), appreciable amounts of mercury can go into solution when ground waters react with cinnabar or other mercury minerals, but this is removed almost completely when the solution is passed over mudstones. This is in accord with data of Dall'Aglio (1968) and with the experiments of Krauskopf (1956), who showed that mercury is removed almost quantitatively from sea water by adsorption on Fe(OH)$_3$ or clay; the analyses of oceanic manganese nodules (table 12) and of Mn ores (table 11) suggest that hydrous manganese oxides also act as collectors of mercury.

It has long been known that some hot springs deposit cinnabar and metacinnabar; the conditions of formation have been discussed by White (1955), Tunell (1964), and by Ozerova and others (1969). In addition to the data in table 15, White (1955) quotes a report of 5,200 ppb Hg in hot spring water

from New Zealand, and White and Roberson (1962) report 20 and 200 ppb Hg in hot springs at Sulphur Bank, Calif.; but most such waters that have been analysed did not contain detectable amounts of mercury.

Industrial pollution, notably by alkali-chlorine plants using the mercury cell method and by the paper pulp industry, has been referred to extensively in recent newspaper accounts. The mercury is apparently removed in large part by adsorption on clayey sediments and on hydrous oxides of iron and manganese and also by algae and plankton.

MERCURY IN THE ATMOSPHERE

The available data are given in table 15. The lowest figures presumably represent unpolluted air, which apparently contains less than 1 to perhaps 10 ng/m³ Hg. "Natural pollution" caused by the volatility of mercury from ore deposits of mercury or base metals gave values up to 62 ng/m³. It is evident, however, that much higher concentrations and very large amounts of mercury reach the atmosphere from volcanic emanations, including those from mud volcanoes.

The effects of industrial pollution probably account for the highest figures reported in table 15 for air from California, the Chicago area, and the Moscow-Tula region. The most probable source is the burning of coal and perhaps of petroleum. Another probable source is from metal smelters. It is well known that ores of lead, zinc, copper, and other metals are enriched in mercury and it seems likely that much of the mercury present escapes from the stacks during smelting operations. No data are available, however, either on the amounts of mercury discharged or on its time of residence in the atmosphere.

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Analyses of 28 igneous rocks are given.

Aidin'yan, N. Kh., 1963, Content of mercury in some natural waters: Akad. Nauk SSSR, Trudy Inst. Geol. Rudn. Mestorozhd., Petrog., Mineral., Geokhim. 70, p. 9–11 (in Russian); Chem. Abs. 57, p. 16500, 1962.

Colorimetric analyses gave 0.1 to 0.8 μg/l Hg (avg. 0.1 μg/l) in 21 rivers, European SSSR. Fourteen waters from seas and oceans gave 0.7 to 2.0 μg/l Hg (avg. 1.3 μg/l).

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Aidin'yan, N. Kh., and Belavskaya, O. A., 1963, The problem of supergenic migration of mercury: Akad. Nauk SSSR, Trudy Inst. Geol. Rudn. Mestorozhd., Petrog., Mineral., Geokhim. 99, p. 12–15 (in Russian); Chem. Abs. 59, p. 8171, 1963.

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Analyses are given of 38 waters drained from cultivated soils and of four river waters; 38 samples showed 0.02–0.07 µg/l Hg (avg. 0.05 µg/l Hg), two showed 0.2 µg/l.

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Ground waters of the region and mine waters were low in Hg (<0.5–5 µg/l).

MERCURY CONTENT OF ROCKS, SOILS, AND STREAM SEDIMENTS

By A. P. Pierce, J. M. Botts, and H. E. Learned

Mercury is routinely determined in U.S. Geological Survey laboratories with atomic absorption equipment developed by Vaughn (1967). An independent check by J. H. McCarthy, Jr., of this method against the method of neutron activation is summarized below:

Determination of mercury in parts per billion in U.S. Geological Survey rock standards

Investigator	Method	Standard rock No.					
		G-1	GSP-1	AGV-1	PCC-1	DTS-1	BCR-1
J. H. McCarthy (in Ehmann, 1968)	Atomic absorption	40	11	17	17	5	7
Vaughn and Learned (1967)	Neutron activation	50	11	17	17	5	7

With the possible exception of standard rock AGV-1, the analyses with two entirely independent methods compare remarkably well, especially considering the rather low mercury content of the rocks.

We have tabulated statistics on mercury content of rocks, soils, and sediments as determined by the atomic absorption method, from three readily available sources: analytical data that are computer stored and that are immediately available for processing, data that have already been published, and data that are in the process of publication and have limited computer availability. All three sources of information contributed to the compilation of table 17 (in the back of this report) in which statistics for about 25,000 samples from 32 areas are listed. Areas represented in table 17 are located in the central and western conterminous United States, in Alaska, and in Puerto Rico. The bulk of the samples were collected in order to test for the presence of anomalous concentrations of metals in surface materials.

A wide range from < 10 to 6,000 ppb mercury, is seen in the modal mercury values listed in table 17. This variability indicates that levels of natural mercury concentrations, or abundance, are relatively complex functions of geologic conditions and that criteria for either mercury mineralization or abnormal mercury contamination should be evaluated separately in any single area of interest.

The modal mercury values canvassed in table 17 also indicate that mercury tends to occur most frequently at certain concentrations. For example, modes at about 50 ppb and at about 200 ppb are especially common. The tendency may be identified both with sample type and with the effects of specific geologic processes, occurring at or near the surface in the area sampled. The common occurrence of mercury ores in concentrations of about 0.1 to 0.5 percent mercury (1,000 to 5,000 ppm) (Lovering, 1969, p. 115) may be another instance of this tendency, although it represents the effects of geologic processes operating under rare geothermal conditions.

The percentile ranges of mercury distributions for the first 18 areas listed in table 17 (see also fig. 1) indicate that for less than 20 percent of the rock samples and stream-sediment samples have concentrations greater than 1,000 ppb mercury. For rocks and stream sediments the upper limit of the ranges of 90th percentiles indicate that any mercury values greater than 1,000 ppb are considered worthy of further investigation as possible results of (1) mercury mineralization processes or (2) surface contamination by mercury-bearing wastes.

Statistics for only four sets of soil samples are available, and these suggest a background value of 500 ppb mercury for soils in Western United States.

These critical values are generalized estimates based on the data in table 17. As mentioned previously, firm criteria for determination of anomalous mercury values should be evaluated individually for each area of interest.

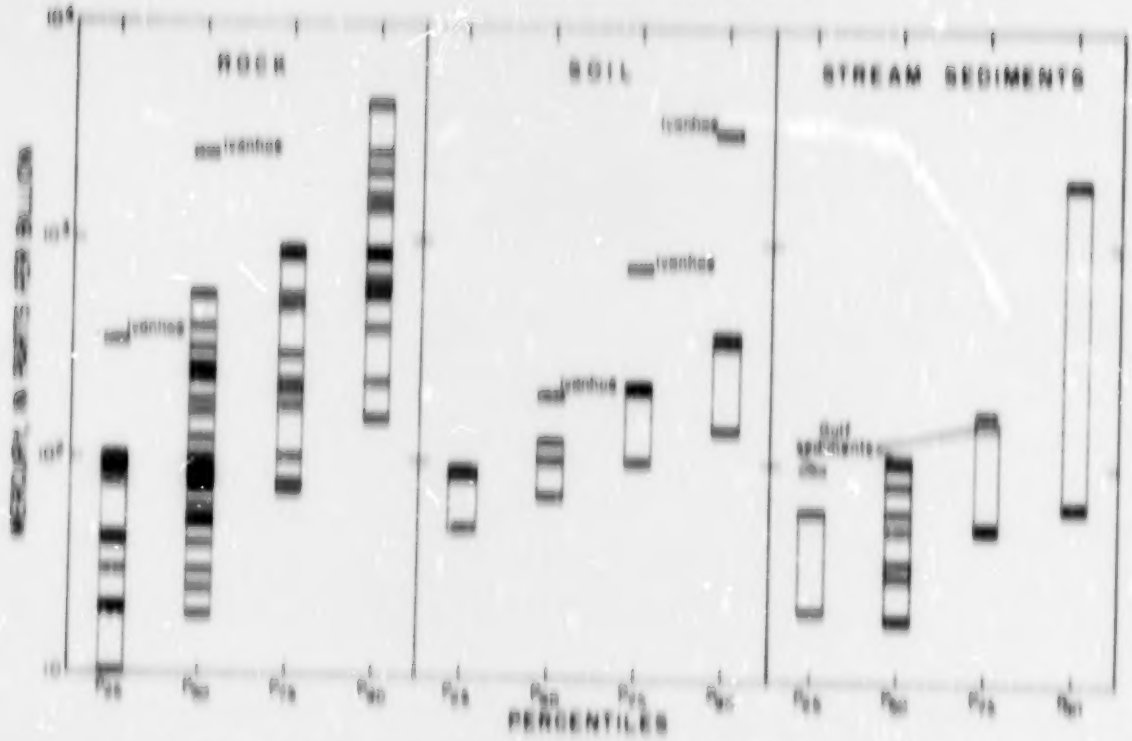

FIGURE 1.—Percentile ranges of mercury distribution in rock, soil, and sediments.

As a frequency distribution approaches normality the arithmetic mean approaches the median. Many of the mercury distributions we have seen approach normality. Therefore, where median values were not available, arithmetic means (table 17) were used as approximations of the median. Where neither arithmetic means nor medians were available, geometric means were used as measures of central tendency. These statistics are listed in the 50th percentile column of table 17 and in the graphical summary shown in figure 1.

We acknowledge the assistance of Lamont T. Wilch, Theodore M. Billings, and Rosa V. Mendes for their aid in the computer processing for this report.

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MERCURY IN SEDIMENTARY ROCKS OF THE COLORADO PLATEAU REGION

By H. A. Cadigan

Mercury content of sedimentary rocks in the Colorado Plateau region ranges from <10 ppb to >10,000 ppb. Sedimentary rocks compose or immediately underlie more than 90 percent of the surface of the region.

Samples have been collected by the author and other Geological Survey employees engaged in various geologic investigations in the Colorado Plateau region over the past 20 years. The major projects involved were the stratigraphic studies program conducted on behalf of the Atomic Energy Commission, 1948–58, and the Geological Survey's continuing Heavy Metals program which began in 1967. Samples collected for studies of mineral deposits or to confirm geochemical anomalies were omitted from this summary.

The data presented here were obtained from 8,012 samples collected from surface outcrops at approximately 150 localities in the Colorado Plateau region (fig. 1). The samples were analyzed in the laboratories of the U.S. Geological Survey by means of an atomic absorption technique.

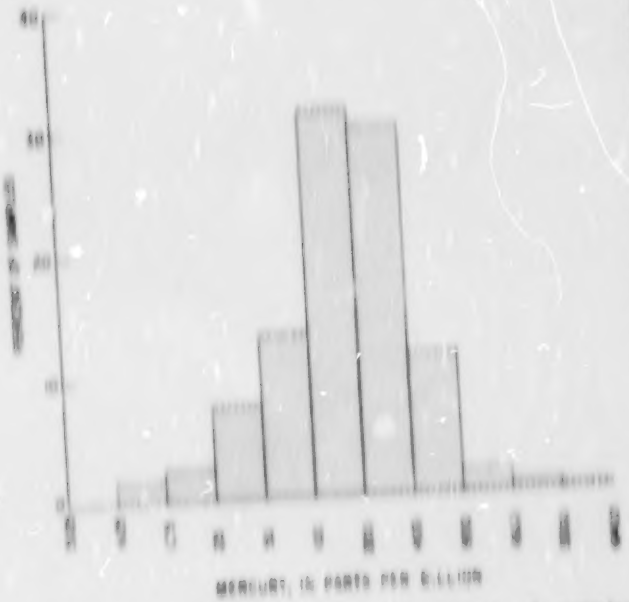
Data on mercury content of most of the major sedimentary stratigraphic units are summarized in table 18, in the back of this report. Statistics are listed under the following headings: "Number of samples," the number of analyses on which the computed statistics are based; "Median," the middle value of each distribution (half of the values are larger and half are smaller); "Highest," the maximum value determined; "Lowest," the minimum value; and "Middle 68 percent of samples," the range of values grouped around the median, approximately ±1 percent (one standard deviation) on each side. "Dominant rock types" refers to the textural rock type listed below in order of importance and which makes up 90 percent or more of the formation or the group. "Approximate average thickness" is given to provide an idea of the order of magnitude of the amount of rock involved. The statistical distributions of mercury values are approximately log normal.

FIGURE 1.—Location of Colorado Plateau region (stippled)

The stratigraphic units are listed in table 18 in order of youngest to oldest; not all units are present in all parts of the region. Their absence is due to erosion or nondeposition. The Duchesne River Formation is present and was deposited only along the north edge of the region. The Dolores and arkosic facies of the Cutler are present and were deposited only in the eastern part of the region.

As depicted in a series of outcrop maps of many formations in the Colorado Plateau region (Newman, 1968), outcrops of the Tertiary and Upper Cretaceous sedimentary rocks in the region are discontinuous because of erosion, but they occupy approximately 20 and 30 percent, respectively, of the surface area of outcropping sedimentary rocks. Jurassic and Triassic rocks crop out in approximately 40 percent of the sedimentary rock surface area and Paleozoic rock outcrops (Permian, Pennsylvanian, and others) occupy the remaining 10 percent.

The average distribution of mercury in the sedimentary rocks which form the surface or which immediately underlie soil-covered surfaces of the Colorado Plateau region is shown in figure 8. The figure



MERCURY, IN PARTS PER BILLION

FIGURE 5.—Frequency histogram of percent of samples plotted over mercury content—a composite of the formation and the group sample data summarized in table 18, weighted for area of outcrop and unit thickness. Basal scale is logarithmic. The statistics for mercury content of Colorado Plateau sedimentary rocks are as follows: Median, 100 ppb; maximum >10,000 ppb; minimum <10 ppb; range of middle 68 percent of samples, 66–870 ppb.

is a composite of values of the samples used for table 18, weighted in terms of the proportions of the rocks by geologic period composing the surface outcrops and in terms of thickness of individual units. It is thus a rough generalization, but it is based on the best information available at the moment. The Tertiary contribution to the average is computed using the three units listed in table 18. The Duchesne River unit is given a weight of 2 for the proportion of Tertiary rocks and a thickness weight of 0.13 (thickness of the Duchesne River divided by total thickness of the Tertiary units). The Uinta and Green River unit is given a weight of 2 for the Tertiary and a thickness weight of 0.7; and the Wasatch and Colton unit is given a weight of 2 and a thickness weight of 0.17. The units in the other periods are treated similarly with the Cretaceous receiving a weight of 8, the combined Jurassic and Triassic receiving a weight of 4, and the combined Permian and Pennsylvanian units receiving a weight of 1.

Samples containing the highest mercury content (>10,000 ppb) were collected in mineralized areas near uranium deposits in the Morrison, Entrada, Chinle, and Moenkopi Formations. The maximum mercury content has not been determined in these areas, nor has the three-dimensional pattern of occurrence. Most of the samples from the Morrison and Chinle which contain more than 1,000 ppb mercury were collected from localities near known uranium deposits. Stream-sediment samples collected from streams adjacent to and draining the mineralized areas have been found to contain as much as 1,100 ppb mercury. Samples from the Green River oil shale strata also contain higher amounts of mercury (1,000 ppb).

No significant correlation appears to exist between mercury content and rock texture per se in Colorado Plateau sedimentary rocks. For example, mercury is present in the Navajo Sandstone in lower quantities than in any of the other formations. Regional distribution of mercury in the Navajo was previously studied (Cadigan, 1969). The Wingate Sandstone, similar in structure to the Navajo, and only slightly finer grained and slightly less well sorted, contains substantially higher amounts of mercury than the Navajo. This example suggests that factors other than texture may exert a higher level of control of the abundance of mercury in formations. There is certainly a strong suggestion that rocks that are predominantly composed of altered volcanic detritus, such as the mudstone strata of the Wasatch, Colton, Morrison, and Chinle Formations, contain higher amounts of mercury than do the rocks that contain little volcanic detritus.

Limestones in the Hermosa and Rico Formations contain more mercury than the values given in the literature (Turekian and Wedepohl, 1961).

Studies of the distribution of mercury and other metallic elements in Colorado Plateau sedimentary rocks are continuing and may yield additional information to modify or supplement data and conclusions presented in this report.

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CHEMICAL BEHAVIOR OF MERCURY IN AQUEOUS MEDIA

By JOHN D. HEM

The chemical behavior of the element mercury in water is highly interesting, although rather complicated and still not entirely explainable. Its behavior is "mercurial" in more than one sense of the word. A general statement of what is known and can reasonably be inferred about the aqueous chemistry of mercury is given here. This review should aid in the interpretation of analyses for mercury in surface and ground water and may help predict what will happen when mercury is added to river or lake water in waste-disposal procedures.

OXIDATION AND REDUCTION BEHAVIOR

Under the usual conditions of temperature and pressure that occur in river and lake water and water-saturated sediment, mercury can be present in one or more of three different oxidation states. The most reduced, in a chemical sense, of these forms is the metal, which is a liquid at ordinary temperatures and which has a distinct tendency to vaporize. The other two forms are ions; the more reduced of the two ions is the mercurous ion Hg_2^{++}, where the average valence of mercury is +1. In oxidizing conditions, especially at low pH, the stable form is the mercuric ion, Hg^{++}.

Although chemical oxidation does not necessarily require the presence of oxygen, this element is the most common oxidizing agent and systems in contact with air tend to be relatively oxidized. In the absence of oxygen relatively reducing conditions may become established, permitting the conversion of elements such as sulfur to the sulfide form. The intensity of oxidizing or reducing conditions in a chemical system is usually expressed as an electrical potential, in volts. The more intensely oxidizing systems have positive potentials and reducing systems have negative potentials. By theoretical chemical equations, applicable at equilibrium, the potentials to be expected in water solutions under various chemical conditions can be calculated. The theoretical solubility and stability of many elements can be usefully calculated in a similar way, by considering the interrelationships of oxidation-reduction equilibria and the effects of common anions in forming various compounds.

CHEMICAL THERMODYNAMIC DATA

Chemical research has provided basic data such as equilibrium constants, standard electrochemical potentials, and free energies of formation, for many of the most significant species of mercury that can be present in water. Table 19[1] is a compilation of chemical equilibrium constants and standard potentials that were taken from published literature. Potentials are given only for redox reactions. Data on additional species can be obtained from the compilation of Stillen and Martell (1964). These kinds of data are useful in calculating mercury behavior and solubilities. Table 20 contains standard free energies of formation of the mercury species that are reported in the literature. These permit calculation of the relative stability of different forms of mercury in aqueous media under a wide range of conditions.

STABILITY AND SOLUBILITY CALCULATIONS

As the data in tables 19 and 20 imply, mercury forms many solute species. Some of these are complex ions with a high degree of stability. A calculation of solubility for mercury must take into account a large number of possible forms. This situation is further complicated because of the possible existence of different oxidation states. Mercury in the form of liquid metal is somewhat volatile and can escape from systems open to the atmosphere, and many mercury compounds are somewhat volatile also. Mercury forms many strong organic complexes and is generally much more soluble in organic liquids than in water.

Data from tables 19 and 20 were used in constructing the stability-field diagram, figure 4, which shows the solid and liquid forms of mercury that will be stable in the conditions of pH and redox po-

[1] Tables are in the back of the report.

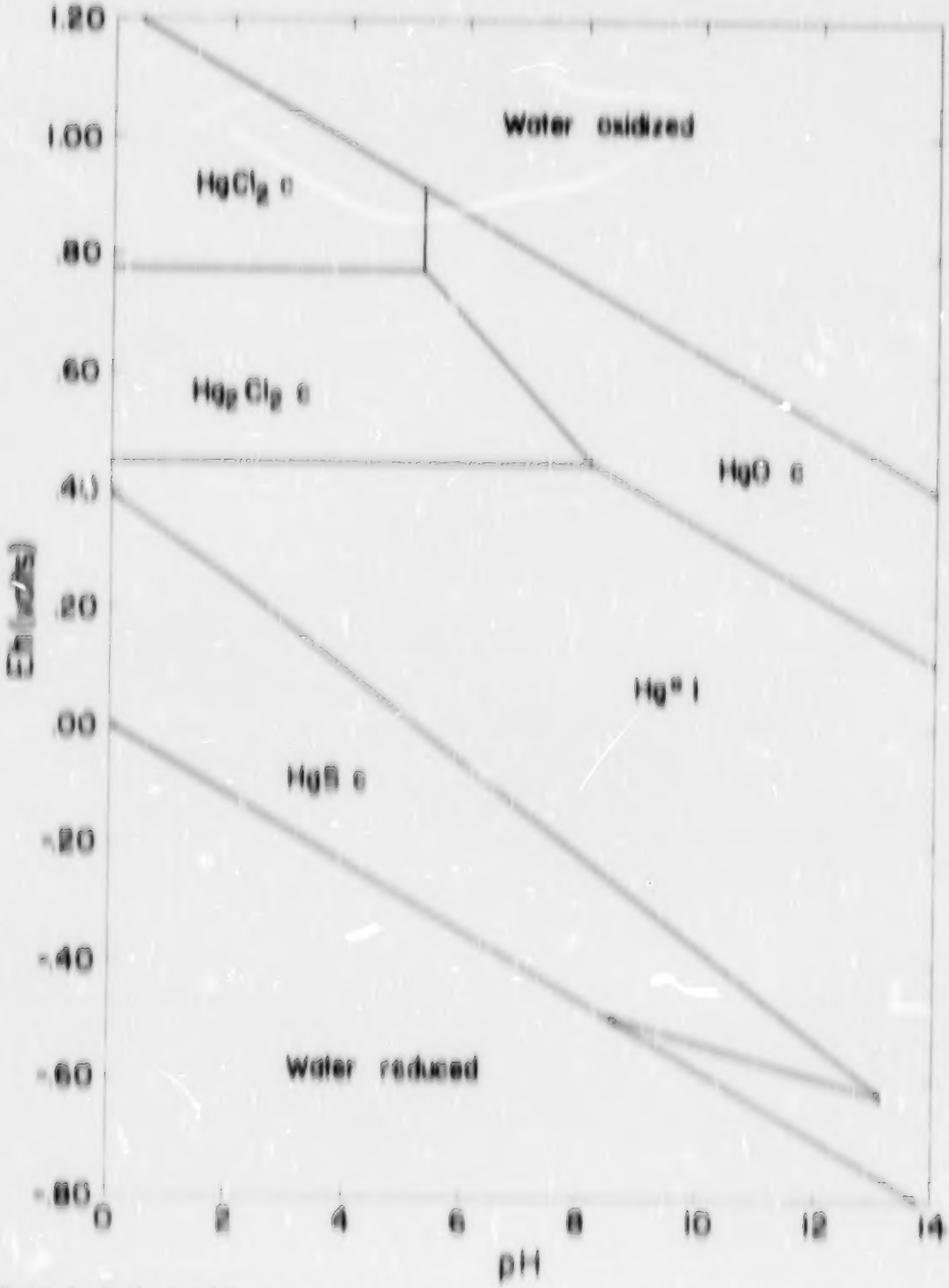

FIGURE 4.—Fields of stability for solid (c) and liquid (l) mercury species at 25°C and 1 atmosphere pressure. System includes water containing 58 ppm Cl⁻, total sulfur 96 ppm as $SO_4^{=}$.

terial under which water itself is chemically stable. The existence of mercuric chloride, calomel, and cinnabar depend on the presence of chlorine and sulfur species in the system. Values arbitrarily selected are 10^{-3} moles per liter of each. This concentration is equivalent to 36 ppm Cl and 96 ppm SO_4^{-2}. No single value for mercury concentration need be specified for locating the boundaries. Calculation techniques used in preparing Eh-pH diagrams have been described extensively in the literature. Solid species are identified by the abbreviation "c", gases "g", liquids by "l", and dissolved species by superscript plus or minus signs or by the abbreviation "aq". The calculations are for the standard temperature of 25°C. Effects of temperatures 10 to 15 degrees above or below this value are probably small enough to be ignored for this type of approximate treatment. Temperature effects may be important in some systems, however.

At the conditions of pH and Eh likely to occur in aerated or anaerobic water (pH 5 to 9 and Eh less than 0.5 volts) the species Hg° liquid and HgS (cinnabar) are the principal ones likely to enter into equilibria affecting the solubility of mercury. The organometallic compound dimethyl mercury for which a standard free energy value is given in table 20 was considered in preparing the stability field diagram. Dimethyl mercury is not thermodynamically stable in the system as specified.

The data in tables 18 and 20 can also be used to calculate the solubility of mercury at equilibrium in the system of figure 4 and to identify the predominant solute species at any area of interest in the diagram. Figure 5 represents the areas of dominance of the solute species that will be stable in the presence of the same levels of chloride and sulfur species as specified for figure 4.

Calculations of solubility of the dominant species also were made in preparing figure 5, and results are given in a general way on the diagram.

The main features of the aqueous inorganic chemistry of mercury under equilibrium conditions are clearly indicated by the two diagrams. Over much of the area of moderately oxidizing conditions above pH 5 the predominant mercury species in solution is undissociated mercury. The solubility of this material is nearly constant over the whole area where the liquid metal is stable, and is relatively low, about 25 ppb as Hg. This represents the likely upper equilibrium limit of mercury in surface streams and lakes that are low in chloride. Studies of this form of aqueous mercury were made by Parland and Archinard (1952).

Mildly reducing conditions, as are likely to occur in many lake and streambed sediments, can cause the mercury to be precipitated as the sulfide, cinnabar. This compound has an extremely low solubility. In the fields of $Mg(OH)_2$ aq and HgS, near neutral pH, the equilibrium solubility of mercury may be lower than .002 ppb. Very strongly reducing conditions, however, may increase the solubility somewhat by converting the mercuric ion to free metal.

In solutions that are high in chloride the solubility of mercury in oxygenated water may be greatly increased by the formation of the uncharged $HgCl_2$ complex, or anionic complexes such as $HgCl_3^-$. The area of dominance shown for chloride complexes would be enlarged if chloride had been increased above 10^{-3} molar. Inorganic mercury complexes in waters in Sweden were reported by Aufalt and others (1968) to include $HgCl^+$, $HgOHCl^0$, and $Hg(OH)_2^0$, with predominant forms depending on chloride concentration and pH. Stability data for the $HgOHCl^0$ species were not given by Wagman and others (1968).

It would appear that mercury concentrations in stream water could be as high as 25 ppb without loss by chemical precipitation. It does not seem that such levels are likely to be common, however, for various reasons, two of which are:

1. Mercury tends to be volatile and will be lost as vapor from the water surface exposed to the air.
2. Most mercury species are much more soluble in organic solvents than in water. Moore and Voight (1957) found, for example, that dissolved free mercury was taken up strongly by organic solvents. When cyclohexane was added to water that contained metallic mercury, the ratio of mercury retained in the water to that in the cyclohexane was only 0.03. This implies a mechanism for removal of mercury from water by aquatic organisms and the effect of organisms is known to be very important.

Mercury that enters reduced sediments can become relatively immobile, so long as a reasonable degree of reduction continues to prevail. At high pH, if much reduced sulfur is present, however, mercuric sulfide anions can become very soluble.

Complexes of mercuric ions with ammonia are described in the literature and some data on one such complex are given in table 19. This complex is not a predominant form of mercury unless the solution

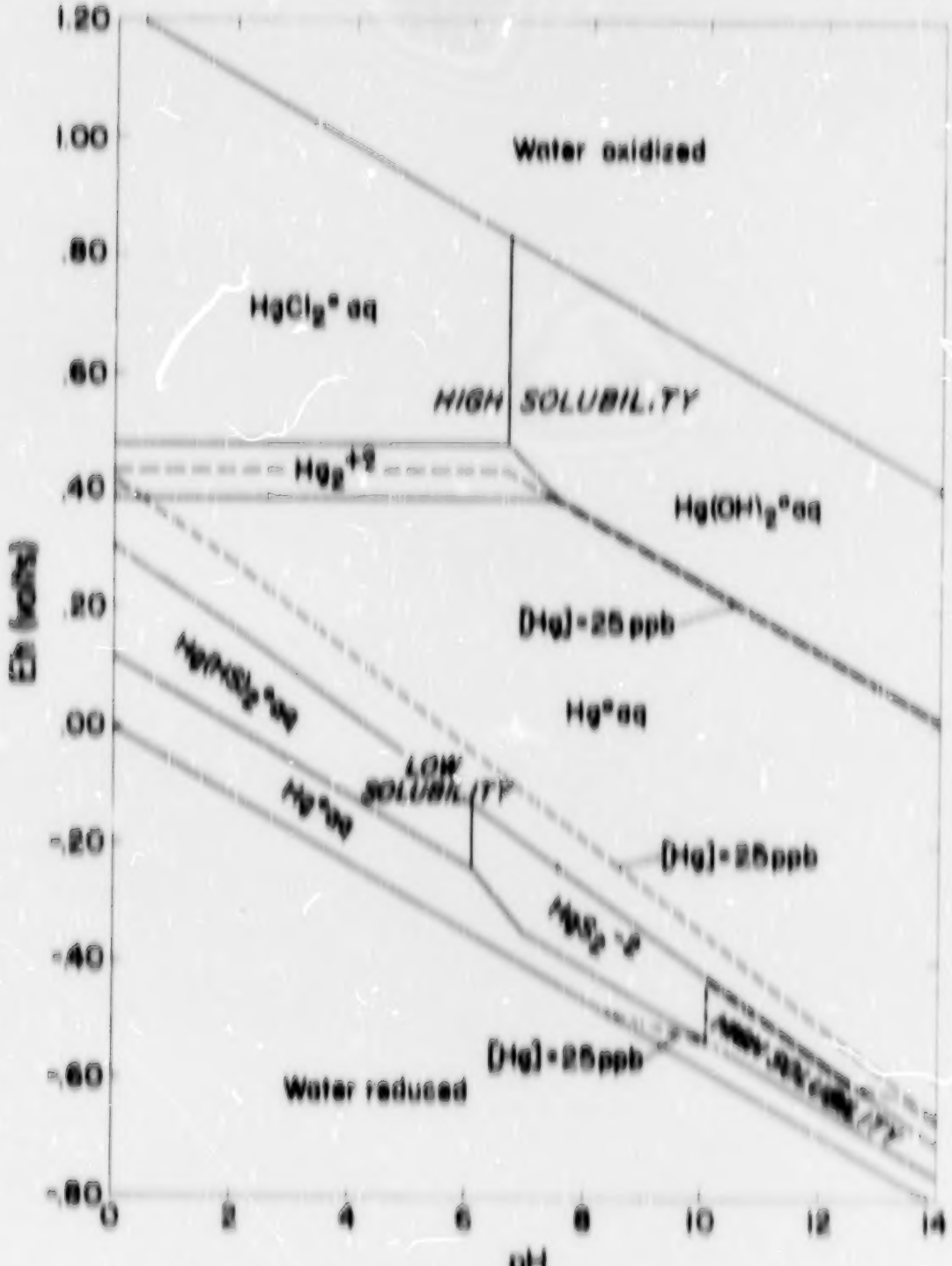

Fig. 6.—Fields of stability for aqueous mercury species at 25°C and 1 atmosphere pressure. System includes water containing 60 ppm Cl^-, total sulfur 96 ppm as sulfate. Dashed line indicates approximate solubility of mercury in this system.

contains more than 100 ppm of NH_4^+, a level seldom attained in natural water.

ORGANIC COMPLEXING EFFECTS

The relative importance of organic solute complexes of mercury in the aqueous chemistry of the element cannot be fully decided at present. The information on such complex species is incomplete and some of it is conflicting. Mercury does form some very strong organic complexes. Some of these are relatively soluble in water. Most forms for which data are readily available, however, might be expected to be altered to other, more stable and generally less soluble, forms in natural water systems. Nevertheless, the fact that a given organic complex is not thermodynamically stable should not be used as a basis for dismissing or ignoring it. Species that are not at equilibrium are commonly found in natural water and can be very important factors in the composition of the solution. Nonequilibrium species are especially likely to be important in surface streams that are used for disposal of wastes, and organic complexes of mercury could be important in these streams.

A particularly significant question arises in connection with the organic complex methyl mercury. The liquid dimethyl mercury is reported in table 20 to have a standard free energy formation of 33.5 kcal (kilocalories) per mole. This value was used in the calculations for preparing figure 4. No region exists in the diagram where $Hg(CH_3)_2$ would be the most stable phase.

Methyl mercuric ion, $HgCH_3^+$, is cited in publications by various authors as the most important form in fish and various other food products of animal origin (Weston, 1967). It has been identified in cultures of methane-generating bacteria to which mercuric ions had been added (Wood and others, 1968). Although the literature has been examined carefully no free-energy value for $HgCH_3^+$ could be found, and no firm basis for calculating or estimating such a value seems to be available. This species could not be considered in constructing figure 5.

In the absence of positive information it seems logical to allow for the possibility of finding methyl mercury or other organic complexes in natural water, and these complexes may offer problems to the analytical chemist.

LIMITATIONS OF THEORETICAL EVALUATION

The summary of aqueous mercury chemistry that is obtainable from the Eh-pH diagram and related calculations seems to fit reasonably with what can be observed in the field. However, there are important areas where available information is inadequate to permit full acceptance of the theoretical model without further testing. The frequent departure of natural systems from equilibrium is well known, and must be kept in mind when using equilibrium calculations. There are two aspects of mercury chemistry that are particularly important sources of departure from what can be predicted theoretically. One of these, the formation of organic complexes and participation of mercury in biochemical processes has been mentioned already. However, it has not been proved conclusively that methyl mercury is produced in abundance in sediment by bacterial activity; the energy that the organisms would have to expend is large, which is contrary to most metabolic processes.

A second property of importance is the tendency for mercury to participate in disproportionation reactions—that is, in reactions of the type $Hg^0 + Hg^{++} \rightarrow Hg_2^{++}$. This and similar reactions are well known and provide a means whereby mercury could be converted to the liquid form and escape as vapor. The oxidation and reduction reactions of mercury seem to be less inhibited by energy barriers than those for many other elements, and the course of such reactions may be difficult to predict at times. The combination of oxidized mercuric ion with the reduced sulfide ligand to form cinnabar, for example, is an unusual feature and seems to give a high degree of immobility to mercuric mercury in a reduced environment where it would not normally be expected to occur at all.

Thus, although a good beginning toward understanding of the aqueous chemistry of mercury has been made, a considerable amount of basic research is still needed, especially on rates and mechanisms of reaction and on the behavior of organic mercury complexes.

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MERCURY CONTENTS OF NATURAL THERMAL AND MINERAL FLUIDS

By D. E. White, M. E. Hinkle and Ivan Barnes[1]

VOLCANIC FUMAROLES

Data on mercury contents of fumaroles are lacking because of the rarity of volcanic eruptions and high-temperature fumaroles and, until recently, the lack of adequate methods of analysis. Hawaiian and Alaskan fumaroles should be studied.

GASES

Water condensed from volcanic fumaroles was analysed by Aidin'yan and Ozerova (1962) and was found to contain 0.5–6 ppb mercury. Fumaroles of the lowest temperature (≤100°C) contain the least mercury (≤0.5 ppb); at 220°C, the mercury content is about 1.5 ppb, and at 270°C, it is about 6 ppb. Residual gases (not condensed in water) contain 8×10^{-7} to 4×10^{-5} g/m³ (grams per cubic meter) of gas.

SUBLIMATES FROM FUMAROLES

Sublimates are commonly more enriched in mercury than is vapor; reported contents range from about 10 to >10,000 ppb (Aidin'yan and Ozerova, 1966). Native sulfur, sulfates, and ammonium chloride have the highest reported mercury contents.

HOT SPRINGS

The relationships of hot springs to mercury deposits have been studied by Brannock (1948), White (1955, 1967), White and Roberson (1962), and Dickson and Tunell (1968). Some springs of special interest are also discussed by Barnes (1970). Efforts to determine the mercury contents of the fluids of these springs were not notably successful until 1966, when effective analytical methods were developed by the U.S. Geological Survey (Vaughn, 1967; Hinkle and Learned, 1969).

We have recently analysed thermal and mineral waters by amalgamating mercury on silver in acid solution. The silver-mercury amalgam was heated in an induction furnace and the mercury vapor determined in a mercury vapor detector by photo absorption. The detection limit is 0.01 ppb. The results are given in table 21.[2]

[1] Incorporates data from W. W. Vaughn, Howard McNerthy, F. N. Ward, and R. O. Fournier and background data from the literature, mainly Russian.

GASES

The hot spring gases at Coso Hot Springs, Calif., have been shown to be enriched in mercury (Dupuy, 1948; White, 1955; Dickson and Tunell, 1968), but concentrations were not determined precisely. Superheated steam from steam wells at The Geysers, Calif., contains a measurable amount of mercury. An early analysis of condensed steam showed a content of 130 ppb Hg (White, 1967, p. 590), but this value is almost certainly too high. Condensed steam from the McKinley steam field at Castle Rock Spring, Lake County, Calif., contains 1 to 8 ppb mercury (table 21). The mercury content of hot-spring gases is not adequately known and needs detailed study.

WATERS

R. L. Wershaw, in this report, summarizes data that suggest that the natural mercury content of unpolluted rivers in areas where the rocks have a normal mercury content is less than 0.1 ppb. The mercury contents of water closely associated with mercury deposits, reported prior to 1966, are summarized by White (1967). Although various analytical procedures were used, these values are probably much too high—they range from <20 ppb (stated detection limit) to 400 ppb. In contrast, recent analyses of the same type of water range from <0.05 to 20 ppb mercury.

Tentative generalizations on mercury contents reported from the thermal and mineral waters of the northern California Coast Range are: (1) Waters that are low to moderate in salinity (<5,000 ppm total solids) and in temperature (<40°C) are nearly always low in mercury (<0.05 ppb); (2) cool waters of high salinity tend to have higher mercury concentrations (table 21) such as 0.1 ppb (Bali Spring north of Wilbur Springs) and 1.5 ppb

[2] Tables are in the back of the report.

(Complexion Spring); (3) hot, dilute waters (table 21) are low in mercury; (4) the hot, moderately saline waters (table 21) of Sulphur Bank and the warm saline Wilbur Springs contain about 1.5 ppb mercury; (5) the mercury content of most of these waters exceeds the contents obtained by the U.S. Geological Survey for relatively unpolluted river waters. (See R. L. Wershaw, "Sources and behavior of mercury in surface waters," this report.) Solid materials (table 21) depositing from the fluids seem to retain mercury.

Agua de Ney Spring of Siskiyou County, Calif., is remarkable for its high salinity, pH, and sulfide content (Feth and others, 1961); its mercury content is 20 ppb (J. H. McCarthy, written comm., 1966) but no mercury minerals have been identified. The silica-magnesia gel deposited from Agua de Ney contains 500 ppb mercury. In contrast, the cinnabar-depositing Amedee Springs of Lassen County, Calif., contain only 2 ppb mercury (J. H. McCarthy, written comm., 1966).

Mercury contents are reported in table 22 for 17 thermal waters in Yellowstone National Park, Wyo., which is an area that has been affected by extreme volcanic activity of Pleistocene age, with present total heat flow of at least 30 times the world average. The thermal waters have relatively low dissolved solids content but are high in temperature. Mercury contents of water of the major geyser basins are all close to 0.1 ppb; Cinder Pool in Norris Basin has the highest content, 0.28 ppb. The Sylvan Springs area in Gibbon Basin, Yellowstone National Park, has higher mercury contents than most other Yellowstone National Park waters; four analyses range from 0.2 to 0.5 ppb.

PRECIPITATES FROM THERMAL FLUIDS

Cinnabar and metacinnabar are precipitating from the thermal waters of Sulphur Bank and Amedee Springs, Calif., Steamboat Springs, Nev., and Boiling Springs, Idaho (White, 1967; Dickson and Tunell, 1968). Sulphur Bank is the most remarkable of the four, having produced more than 5,000 tons of mercury before mining operations ceased, which is the highest yield in the world from a deposit clearly formed from hot springs (White and Roberson, 1962). According to White (1967) only a little cinnabar is precipitating from vapor escaping from natural vent areas of The Geysers geothermal steam system of California. No mercury minerals have been recognized in Yellowstone National Park thermal spring precipitates.

Precipitates and bottom sediments in many hot springs, even where no mercury mineral is evident, contain quantities of mercury much above the average content for crustal rocks. (Michael Fleischer, Oslo report), which provides evidence for mercury transportation and concentration from the associated fluids. Reported contents of mercury-enriched sediments in addition to those in table 21 include: Steamboat Springs, 12,000, 150,000, 200,000 and 500,000 ppb; elemental sulfur "cinders" of Cinder Pool, Norris Basin, Yellowstone National Park, 50,000 ppb; and silica from Primrose Spring of Sylvan Springs, Gibbon Basin, Yellowstone, 5,000 ppb; and elemental sulfur precipitated from condensed steam of P.G. & E. powerplant No. 2, The Geysers, California, 5,000 ppb.

The fine-grained muds of the mudpots and mud volcanoes of Yellowstone National Park commonly show similar concentrations. Nine analyses show a range of 5,000 to 150,000 ppb. These muds are products of hydrothermal alteration of adjacent rocks; the only reasonable mechanism for enrichment in mercury is condensation from the hot vapor that streams up through these muds (White and others, 1970). Some steam and much of the mercury evidently condenses in the surface pools. Even though Yellowstone National Park fluids are now in mercury, as compared to those of other areas, they are transporting and depositing measurable quantities of mercury.

Large mercury anomalies have been found by Dall'Aglio and others (1966) in stream sediments around the Italian geothermal steam fields of Larderello and Monte Amiata; more than 50 percent of all their analyses ranged in mercury content from 200 to 50,000 ppb. Most anomalies could not be traced to mercury deposits and are interpreted as indicators of geothermal steam. Transportation by vapor appears to be the most logical explanation.

PETROLEUM, NATURAL GAS, AND OIL-FIELD WATERS

Only a few waters associated with petroleum have been analyzed for mercury; contents reported from the Cymric oil field, Calif. (Bailey and others, 1961; White, 1967), range from 100 to more than 300 ppb, but these are probably too high and should be redetermined by current methods of analyses. Mercury analyses of Cymric crude oils range from 1,000 to 21,000 ppb, which is in the range of elemental mercury solubilities in hydrocarbons (Spencer and Voight, 1962). The natural gas of the Cymric field is saturated with mercury vapor, thus indicating saturation with elemental mercury. During transport in a pipeline, mercury vapor evidently

combines with H_2S from "sour" gases of other oil fields and is precipitated in the pipelines. Native mercury separates from the crude oil at the local pumping station. Total mercury yield from all the fluids is unrecorded from the field but may be in the order of hundreds of tons.

Petroleum and tarry residues containing mercury (table 23) are associated with the mercury deposits of the Wilbur Springs district. Light petroleum of the "froth veins" of the Abbott mine (White, 1967) contained 100,000 ppb mercury. Tarry petroleum, probably residual from loss of the lighter hydrocarbons, contained 500,000 ppb. Hydrocarbons extracted from fault gouge from the Abbott mine by organic solvents contained 1,000 to 5,000 ppb, but a sample of petroleum that had flowed from a new underground working and was stored for several years prior to analysis contained only 500 ppb. Tar from the nearby Wilbur oil test well (table 23) contained 1,000 ppb mercury.

Some additional evidence for enrichment of mercury in fluid hydrocarbon deposits is indicated by the mud volcanoes of the Kerch-Taman territory of the U.S.S.R. (Karnaukh and Morozov, 1966). Mud and other debris that were extruded with hydrocarbon gases and waters of the oil-field type are enriched in mercury by about 100 times the mercury contents of Tertiary argillaceous rocks.

SUMMARY

Dilute thermal springs contain readily detectable mercury. The springs include high-temperature waters of Yellowstone National Park, which are closely associated with extensive Pleistocene volcanism. Some California thermal waters, and nonthermal waters of appreciable salinity (>5,000 ppm total dissolved solids) but not closely associated with volcanism, contain mercury in the range of 1 to 3 ppb, concentrations notably higher than Yellowstone National Park waters. Sediments associated with some of these springs are rich in mercury, containing about 50 to 5,000 times the mercury content of ordinary rocks (Fleischer, this report), and the mercury contained is presumed to have been transported by the spring water.

Of the natural fluids examined, petroleum and especially the tarry residues of petroleum contain the highest determined mercury contents; available analyses show a range from 500 to 500,000 ppb or from about four to six orders of magnitude above most thermal waters. In the formation of some mercury deposits, petroleum and hydrocarbon gases apparently played a role, but the origin and nature of the fluids that have formed most large mercury deposits are not yet clearly understood. Our data are incomplete for hot springs and volcanic gases, especially in view of anomalous contents of mercury in associated solid phases which indicates vapor transport.

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SOURCES AND BEHAVIOR OF MERCURY IN SURFACE WATERS

By R. L. Wershaw

NATURAL LEVELS OF MERCURY IN SURFACE WATERS

Before one declares a water body polluted with waste mercury from man's activities, it is necessary to know the natural background level of the metal. The data in table 24[1] were obtained on water samples collected for this purpose by district offices of the U.S. Geological Survey, in cooperation with the Federal Water Quality Administration, during May, June, and July 1970. These samples were analyzed for dissolved mercury using a silver wire atomic absorption method discussed by F. N. Ward (this report). The 78 samples, representing surface waters in 31 states, range in concentration from less than 0.1 to 17 ppb. Of the total, 34 contained less than the detectable concentration (0.1 ppb). Of the remainder, 27 samples ranged from 0.1 to 1.0 ppb and 10 samples ranged from 1.0 to 5.0 ppb. Only two samples contained more than 5.0 ppb, the Public Health Service limit for potable water supplies. The fact that many of the samples were taken in areas of suspected mercury contamination would appear to indicate that mercury concentrations in surface waters generally do not exceed tolerable limits except in the immediate vicinity of waste outfalls.

Table 25 shows that the mercury levels measured in surface waters in other parts of the world generally fall in the same low range of values as found in the United States. For example, studies of Dall'Aglio (1968), Heide, Lere, and Rohm (1957), and of Stock and Cucuel (1944) show that natural mercury contents of unpolluted rivers in areas where mercury deposits are not known, are less than 0.1 ppb; this is in general agreement with data presented in table 24 for U.S. rivers.

Samples from rivers draining mercury deposits are known to have natural mercury contents exceeding 5 ppb. Rivashnevskaya and Shabbievskaya (1966) found mercury minerals in the suspended particulate matter of the Vagnob-Dar'ya River 15 to 35 kilometers downstream from mercury ore deposits. Dall'Aglio (1968) measured mercury concentrations as high as 156 ppb in Italian rivers which drained basins having worked and unworked mercury deposits (table 25). Mercury concentrations in these waters were found to decrease as a function of distance downstream from the mercury deposit. Oil field brines as well as thermal and mineral fluids in general (D. E. White and others, this report) and Karnath, Gomcharov, and Vasilevskaya (1965) may contain high mercury concentrations which can be a source of pollution to surface and ground waters. The fact that the oceans contain an estimated 50 million metric tons of mercury suggests that small amounts of the element always have been present in surface waters.

INDUSTRIAL PRODUCTION

The potential for waste mercury contamination of surface waters can be judged in part from a study of the use pattern of mercury by industry. The world production of mercury in 1968 was 9,000 metric tons, of which the United States produced only 1,000 metric tons from mines located principally in California, Nevada, Idaho, and Oregon. The United States imported 800 metric tons of mercury in 1968 so that together with imports and seven hundred tons of reclaimed mercury domestic use amounted to about 2,500 metric tons during that year. During the period 1930–70, the total mercury mined in the United States was 81,000 metric tons and 30,000 metric tons were imported. It is estimated that as much as 25 percent of this total may have been leaked to the environment.

INDUSTRIAL USES

Table 26 gives data for mercury consumption by various users in the United States during the calendar year 1969. The largest commercial consumption occurred in the manufacture of chlorine and caustic soda, a process thought to introduce appreciable amounts of waste mercury in to the environment. For example, Lofroth and Duffy (1969) estimated

[1] Tables are in the back of the report.

that eight chlorine factories in Sweden lose from 25 to 35 metric tons of mercury per year. Mercury losses from such operations have been reported in the United States (Chemical and Engineering News, 1970a) although considerable effort now is being made to reduce their losses of mercury (Chemical and Engineering News, 1970b).

The second largest consumptive use of mercury is in the manufacturing of electrical apparatus. Mercury also finds very widespread use as a fungicide, bactericide, and slimicide. For example, the paint industry uses phenyl mercuric compounds for mildew-proofing and mercury organic compounds are used as seed dressings in agriculture. Mercury compounds are also used in the paper industry to prevent fungal growth in stored pulps and to prevent the growth of slimes in machinery. Because of this, some papers are not used in food packaging (Lutz and others, 1967). Mercury compounds also are employed to a limited extent as catalysts in the production of many organic materials in pharmaceutical and dental preparations, and, because of its conductive properties in the liquid state, in a variety of industrial control instruments.

INDUSTRIAL POLLUTION

The wide variety of uses of mercury by man has resulted in significant mercury pollution of natural water bodies in many parts of the world. If industrial outfalls are not properly scavenged for mercury, or if mercury-bearing materials are improperly disposed of, some of the waste inevitably finds its way into surface waters. For example, Andersson (1967b) measured mercury concentrations of 6 to 29 ppb (dry weight) in sludge from Swedish sewage-treatment plants. Obviously, care must be exercised in the disposal of such sludge to avoid contaminating water resources.

During the summer of 1970, the U.S. Geological Survey analyzed more than 500 water samples representative of industrial effluents and outfalls where mercury contamination was suspected. This work was done in cooperation with the Federal Water Quality Administration. Of the more than 500 samples, 38 percent had less than detectable (0.1 ppb) mercury concentrations; an additional 55 percent contained between 0.1 and 5 ppb. In other words, 93 percent of all the samples analyzed had concentrations which were within the range of Public Health Service mercury content allowable for drinking water supplies despite the fact they represented industrial areas. An additional 1½ percent of the samples had mercury contents ranging between 5 and 100 ppb. Less than 5 percent had concentrations greater than 100 ppb and only two samples of the total had concentrations greater than 10,000 ppb.

Sediment samples from the Missouri River basin were also analyzed for mercury content. Of the 15 samples studied, 11 had mercury contents ranging between 40 and 170 ppb. The remaining four had concentrations of 900, 1,800, 3,000, and 37,000 ppb.

CONCLUSIONS

Natural surface waters contain tolerably small concentrations of mercury except in areas draining mercury deposits. Industrial, agricultural, scientific, and medical uses of mercury and mercury compounds introduce additional mercury into surface waters. Whatever its source, the concentration of mercury compounds, dissolved or suspended, is reduced rapidly by sorption and by complexing reactions with clays, plankton, colloidal proteins, humic materials, and other organic and inorganic colloids (J. D. Hem, E. A. Jenne, this report.) These reactions tend to keep the concentration of dissolved mercury at levels near the normal background except at points of actual mercury discharge.

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BIOLOGICAL FACTORS IN THE CHEMISTRY OF MERCURY

By PHILLIP E. GREESON

FLOW OF MERCURY THROUGH AQUATIC FOOD CHAINS

The living organisms in an aquatic community represent an assemblage of groups, called trophic levels, that are classified according to food utilization. The size of an aquatic community is dependent upon the availability of food materials and its transport through the various groups.

The ultimate basic food substances are the inorganic materials dissolved in the water or the insoluble materials that can be readily converted to bodily needs. The chlorophyll-bearing phytoplankton and higher plants are the principal organisms for conversion of these ultimate basic materials to living matter. They, therefore, are called the primary producers of the system and all other organisms depend upon their existence.

Those organisms that feed upon the plants, such as zooplankton, insects, snails, and small fish, are known as primary consumers. Secondary consumers feed upon the primary consumers and are represented by the larger fish, such as trout, pike, bass, and salmon. Every organism in an aquatic community may, by death and decomposition, contribute directly to the dissolved materials, or may be consumed as food by other organisms. Micro-organisms are responsible for the breakdown of organic materials and the releasing of dissolved substances for reuse. Figure 8 is a simplified representation of the flow of materials through an aquatic food chain.

Although mercury is not considered to be an essential food material for organisms, it is incorporated into the body of the organism by virtue of its presence in the water. Mercury in living tissues is believed to be largely organic and primarily methyl mercury (Weston, 1967). Jenson and Jernelov (1969) indicated that much of the inorganic and organic mercurial wastes from industrial effluents are converted by anaerobes into methyl mercury, CH_3Hg^+, or dimethyl mercury, $(CH_3)_2Hg$. This finding was confirmed by Wood, Kennedy, and Rosen (1968), who stated that the methylation of mercury is due to bacterial activity. The latter authors concluded that dimethyl mercury is the ultimate product but that in situations where an excess of mercuric ion (Hg^{++}) exists, methyl mercury is also produced.

Dimethyl mercury, although stable in alkaline solutions, dissociates to ionic methyl mercury at low pH values. Such low pH conditions may sometimes exist in the anaerobic bottom muds of streams and lakes. Methyl mercury, being soluble in water, is available for incorporation into the body tissues of organisms in the aquatic environment and secondarily into terrestrial predators, such as man. Methyl mercury tends to concentrate in living tissue and at critical concentrations can be extremely toxic.

The concentration of mercury by living things may come by way of the food chain or by direct assimilation from the surrounding medium (Rucker and Amend, 1969). In either event, when mercury is introduced into a food chain, it becomes available to all organisms of the chain.

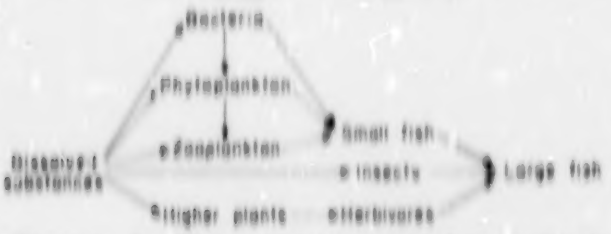

FIGURE 8.—Simplified representation of the flow of materials through an aquatic food chain.

TOXICITY

Mercury compounds inhibit the growth of bacteria, thus their long-standing use as antiseptics and disinfectants. It is to be expected, therefore, that at some concentration mercury compounds added to a natural water system will have a deleterious effect on the bacteria of the system. Mercuric chloride at a concentration of 610 ppb was reported by Hermann (1959) to cause a 50-percent decrease in the 5-day utilization of oxygen by sewage. Ingols

(1954) reported that a concentration of 2,000 ppb results in complete bacteriostasis. The toxicity of mercury to various aquatic organisms is shown in table 27 (in the back of the report).

Mercury in the aquatic environment also is known to have acute effects on the primary producers, but there is not complete agreement on toxic levels. Studies by North and Clendenning (1958) and Clendenning and North (1960) indicated that 100 ppb of mercuric chloride caused a 50-percent inactivation of photosynthesis in the giant kelp *Macrocystis pyrifera* during a 4-day exposure. A concentration of 500 ppb caused a 15-percent decrease in photosynthesis in 1 day and complete inactivation in 4 days.

Ukeles (1962) reported 0.6 ppb of ethyl mercury phosphate as the threshold concentration for inhibiting the growth of marine phytoplankton and that 60 ppb was found to be lethal to all marine species. Burrows and Combs (1958) concluded that ethyl mercury phosphate was an effective algicide at 1,000 ppb. In contrast, Hooper (1960) reported that the threshold of lethal concentrations of mercury salts for phytoplankton ranged from 800 to 60,000 ppb.

Clendenning and North (1960) reported that mercury was found to be more toxic to aquatic organisms than copper, hexavalent chromium, zinc, nickel, or lead. Corner and Sparrow (1956) emphasized that the toxic effects of mercury salts are increased appreciably by the presence of copper.

Chmoschenko (1960) showed that the accumulation of mercury by the marine diatom *Chaetoceros costatum* was largely by passive surface adsorption with limited uptake by metabolic processes. He stated that it is not important whether the primary producers concentrate mercury by active uptake or by passive surface adsorption in the transfer to higher trophic levels.

Chmoschenko's studies of mercury accumulation illustrate an important ecological principle. Aquatic organisms, as well as man, will concentrate mercury within their bodies when the intake rate exceeds the elimination rates. The result, under these conditions, is a buildup with time to the extent that the accumulated mercury can become toxic and, eventually, lethal.

Hucker and Amend (1969) studied the accumulation of mercury in fish. They exposed rainbow trout, *Salmo gairdneri*, for an hour a day to nonlethal concentrations of ethyl mercury phosphate. After 10 days, several fish were sacrificed, and their tissues were analyzed for mercury. The results showed the following concentrations in the tissues:

Tissue	Mercury (ppb)
Blood	12,600
Kidney	12,300
Liver	12,700
Brain	10,100
Gonad	4,100
Muscle	7,000

The remaining fish were maintained in mercury-free water. The authors found that after 15 weeks, mercury had been eliminated from all tissues except the liver and kidney, where concentrations had stabilized at 1,800 and 12,300 ppb respectively.

MERCURY POISONING IN MAN

The toxic effects of waterborne mercury to man were emphasized during the early 1950's when about 40 persons out of more than 100 affected in Japan died of the strange "Minamata Disease." Extensive investigations revealed that the deaths were caused by the consumption of mercury-contaminated fish and shellfish obtained from Minamata Bay. The bay had received large amounts of methyl mercury compounds in the waste effluents from a plastics factory (Kurland and others, 1960). Similar mercury contamination of fish has been reported in Sweden and recently in several places in North America, particularly Lake St. Claire.

As a result of these findings a tentative upper limit of 5.0 ppb of mercury in drinking water has been proposed by the U.S. Public Health Service and the same upper limit set in the U.S.S.R. The maximum is thought to be safe for human health when the total probable mercury intake rates of physiological processes, and excretion rates are taken into account. The U.S. Food and Drug Administration has declared that fish and other foods which contain more than 500 ppb of mercury are unsafe for human consumption.

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MERCURY CONTENT OF PLANTS

By Hansford T. Shacklette

There are but few data available upon which to base an estimate of the amounts of mercury that are absorbed by plant roots and translocated to the upper parts of the plants. Apparently, most plants grown in soils that typically are low in amounts of this element contain very little mercury in their tissues. The difficulties of detecting these small amounts by chemical methods has made routine mercury analyses of plant samples impractical for most laboratories. Under certain environmental conditions, however, plant samples may contain larger amounts of mercury that can be readily detected by less rigorous analytical methods. The discussion that follows distinguishes typical chemical environments for plants from those that, because of naturally occurring mercury minerals or contamination by industrial or agricultural practices, contain anomalous amounts of mercury.

PLANTS GROWN IN A TYPICAL ENVIRONMENT

Typical soils that support vegetation contain very small amounts of mercury; Hawkes and Webb (1962, p. 389) reported 30–300 ppb, and Warren and Delavault (1960, p. 537), 10–60 ppb. The few available reports of mercury analysis of plants suggest that this metal is not concentrated to a significant extent, if at all, in the tissues of most plants that grow in these soils. Malyuga (1964, p. 15) stated that the amount of mercury in plants is 1 ppb; this figure is presumed to be an arithmetic mean, but the data upon which this value is based were not given and no other statement was found in the literature of the "average" mercury content of plants.

In a recent U. S. Geological Survey biogeochemical study conducted in Missouri, 190 native trees and shrubs were sampled for chemical analysis. The species studied were post oak (*Quercus stellata* Wang.), over-cup oak (*Q. lyrata* Walt.), white oak (*Q. alba* L.), smooth sumac (*Rhus glabra* L.), winged sumac (*R. copallina* L.), and red cedar (*Juniperus virginiana* L.). Terminal parts of stems (branches, without leaves) of deciduous trees and shrubs, and terminal branches including scalelike leaves of red cedar, were selected for sampling. These plants grew in an apparently "normal" mercury environment. All samples were reported by T. F. Harms, analyst, to contain less than 500 ppb mercury in the dry material. In an associated study of roadside contamination of vegetation and soils in Missouri, 93 red cedar samples were found to contain less than 500 ppb mercury (T. F. Harms, analyst), whereas the mercury content of dry samples of the soils in which these trees were rooted ranged from 10 to 600 ppb (E. P. Welsch, analyst).

PLANTS GROWN IN AN ENVIRONMENT CONTAINING ANOMALOUS AMOUNTS OF MERCURY

Soils overlying cinnabar deposits may contain as much as 10,000 ppb mercury in their A and B horizons (Shacklette, 1965, p. C10). In a study of mercury and other elements in plants that grew over cinnabar veins at Red Devil on the Kuskokwim River, Lower Yukon River district, Alaska, mercury analyses performed by L. E. Patton yielded the following results:

Host genus	Plant part analyzed	Number of samples	Ppb of dry plant
Alder (*Alnus crispa* subsp. *crispa* (Ait.) Hult.)	Stems	1	1,000
Black spruce (*Picea mariana* (Mill.) Britt., Sterns & Pogg.)	Stems and leaves	1	1,000–1,500
Dwarf birch (*Betula nana* L.)	Stems	8	500–1,000
Labrador tea (*Ledum palustre* subsp. *decumbens* (Ait.) Hult.)	Stems	7	1,000–5,500
Spruce (*Picea kamtschatcensis* (Regel)	Stems and leaves	1	3,000
White birch (*Betula papyrifera* subsp. *humilis* (Regel) Hult.)	Stems	4	500–2,000

Mercury, if present, in other samples of these plant species collected in the same area occurred in amounts below the lower detection limit of 500 ppb.

of the analytical method that was used. It is noteworthy that trees whose roots extended through the loess mantle and came in contact with a cinnabar vein (as observed in prospect trenches that were dug) invariably contained measurable amounts of mercury in their branches; the branches of adjacent trees whose roots did not contact these veins contained no detectable amounts of mercury.

Rankama and Sahama (1950, p. 551) stated, "Droplets of metallic mercury have been found in the seed capsules of *Holosteum umbellatum* (jagged chickweed; family Caryophyllaceae) growing on some mercury-rich soils," and further, "Marine algae may concentrate mercury, and some species are found which contain more than a hundred times as much mercury as sea water does. In exceptional cases mercury is concentrated as native mercury in some land plants. Vegetable fats are relatively rich in mercury."

Goldschmidt (1954, p. 278) reported the occurrence of drops of metallic mercury under the moss cover of the forest floor near hydrothermal mercury deposits in the Rhine Palatinate. A U.S. Geological Survey search for evidence of mercury contamination of plants growing adjacent to a mercury smelter at Red Devil, Alaska, by examination of the soil surface under moss mats and by chemical analysis of leaves from trees, revealed none.

Malyuga (1964, p. 95) stated that the possibility of using the biogeochemical method of prospecting for mercury was quite realistic, but that the slow adoption of this method was due to difficulties in determining the presence of mercury in soils and plants.

The toxicity of mercury to plants apparently depends on the chemical state of the element. Very small amounts of volatilized elemental mercury are believed by some horticulturists to be toxic to certain crops, particularly roses, and they do not use mercury thermometers in their greenhouses because of the danger of accidental breakage. Compounds of mercury, in contrast, are widely used in crop production for the control of certain fungus diseases and, if properly used, produce no apparent toxic symptoms in the plants. Shacklette (1965, p. 109–110) reported on examination of plants in the Red Devil area for evidence of mercury poisoning as follows:

> [illegible], presumably, the soil in the vicinity of the mine, mill, and smelter, has been contaminated as a result of several years' operation of these installations; however, both bryophytes (mosses and liverworts) and vascular plants appeared to be remarkably unaffected. Mosses common to the region grow in a cinnabar mill and smelter drainage stream in which metallic mercury could be seen, and plants on a mountain tundra slope immediately adjacent to and on a level with the mercury smelter exhaust stacks appeared undamaged. No undisturbed outcrops of cinnabar that bryophytes could have colonized were found; but cinnabar was found in placer deposits and in rock used to surface a road, as well as around the mine shafts, and it did not appear to have had any effect on the masses growing near it. We exposed some cinnabar outcrops by digging and found tree and shrub roots that were in contact with the mineral. Branches of the plants having root contact contained anomalous amounts of mercury [illegible] yet the plants showed no toxicity symptoms.

The amounts of mercury found in some samples of plants or plant parts that have been treated with mercury compounds may be large, but the analyses alone do not demonstrate whether the element was absorbed into and translocated throughout the plant tissues or occurred only as a surficial residue. Novick (1968, p. 1) stated that mercury compounds are easily absorbed by plants and can be translocated from one part of the plant to another, that mercury fungicide applied to leaves of apple trees may be translocated to the fruits, and that mercury may be moved from potato leaves to the tubers.

SUMMARY

Plants growing in environments that have the normal small amounts of mercury probably seldom exceed 500 ppb mercury in their tissues. In environments that have significantly larger amounts of mercury because of the natural occurrence of mercury-bearing deposits, the plants may contain between 500 and 5,000 ppb mercury in their dried tissues. Much larger amounts of mercury may be found in plant samples as surficial residues or as deposits in the tissues as a result of intentional application of mercury compounds or from contamination.

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MERCURY IN THE ATMOSPHERE

By J. H. McCarthy, Jr., J. L. Meuschke, W. H. Fyfield, and H. E. Learned

INTRODUCTION

Little is known about the abundance and distribution of mercury in the atmosphere. The mercury content of air over scattered mineralized and nonmineralized areas of the Western United States has been measured in a study of the application of such measurements in geochemical exploration for ore deposits. Some of the data have been reported previously (McCarthy and others, 1950); additional data are reported here. Several factors that influence the mercury content of air are discussed.

DATA

The mercury content of air over 15 ore deposits and above four nonmineralized areas is shown in table 38 (in the back of the report). For several localities data are given for mercury in air at ground level and at 100 feet above the ground. In general, the maximum concentration of mercury is found in air over mercury mines, lower concentrations over base and precious metal mines, and still lower concentrations over porphyry copper mines. The concentration of mercury in air over nonmineralized areas ranged from 0 to 0 up to in the areas investigated.

Nacrite (1950) reported that in the mercury mine at Idria, Yugoslavia, the mercury vapor concentration is 1 to 10 up to, and that the concentration of mercury vapor in air at the mercury processing plant is 0 to 0 up to. Burgess (1951) found that mercury vapor in soil air collected from boreholes 1 to 2 meters deep contained 0 to 0 up to. Mercury in collected 1 meter above the surface contained 0 to 0 up to.

The concentration of mercury in air as a function of altitude is shown graphically in figure 7. The [illegible] were collected at Blythe, Calif. The curve for January 1, 1950, that above 600 feet the mercury [illegible] and synthetic observed data collected [illegible] in late April show an opposite [illegible] Figure 7 also indicates that lower values [illegible] obtained in January than in April.

Williston (1950) found similar mercury contents in air in the San Francisco Bay area. This seasonal variation in the mercury content of air is ascribed to seasonal temperature differences.

In addition to seasonal variations in the mercury content of air, there are daily variations, as shown in figure 8. A record of temperature, barometric pressure, and mercury in air at ground level (dashed line) is shown for 2 days. The data were collected at the Silver Cloud mine near Battle Mountain, Nev. The maximum amount of mercury in air is found at about midday; much smaller amounts are found in the morning and in the evening. The barometric pressure curve is typical and reveals a consistent diurnal variation. The pressure begins to fall at 8:00–9:00 a.m. and falls steadily until about 4:00–7:00 p.m.; then it rises steadily through the night. Thus if no atmospheric disturbances exist, the pressure record transcribes an ap-

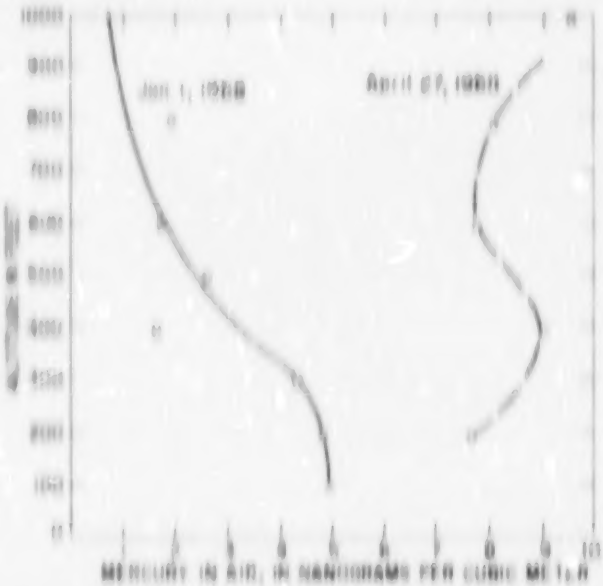

FIGURE 7.—Mercury in air as a function of altitude, Blythe, Calif.

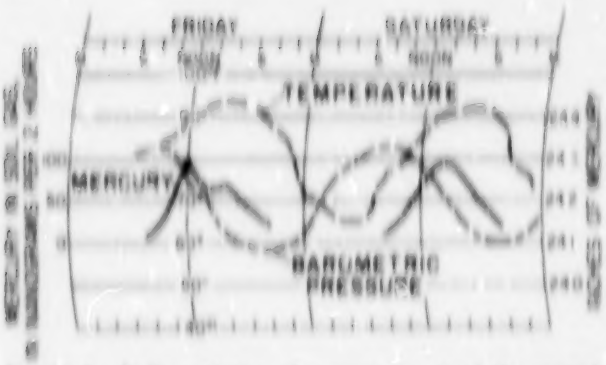

FIGURE 8.—Daily variation of mercury in air at the ground surface, temperature, and barometric pressure, Silver Cloud mine near Battle Mountain, Nev.

proximate sine wave with maximum rate of fall about midday. When the barometric pressure begins to fall, mercury is released to the atmosphere and reaches a maximum when the rate of fall of barometric pressure is greatest.

The mercury content of air was measured at 2-hour intervals for a period of 36 hours at the Ord mine in Arizona. Daytime patterns similar to those at Silver Cloud were observed with a maximum of 600 ng/m³ of mercury found near midday and a minimum of 20 ng/m³ found at 2:00 a.m. The minimum mercury concentration occurred during the time when the rate of increase in barometric pressure was greatest. Thus the daily content of mercury in air is a function of the diurnal change in barometric pressure resulting in the exhalation of mercury through the earth's "breathing process." The effect of temperature is less obvious; the maximum daily temperature commonly occurs 2–4 hours later than the time when maximum mercury is found in air.

Most of the data reported here have been collected on clear days with no precipitation. However, at one sample site near the Ord mine 20 ng/m³ of mercury was found in the air the day before a rainstorm. On the following morning, several hours after the rain, no mercury was detected in the air. Rankama and Rahama (1950) also reported that mercury in the atmosphere is removed by precipitation. Stock and Cucuel (1934) reported an average content of 0.2 ppb of mercury in rain water compared with oceanic abundance of 0.03 ppb mercury.

SUMMARY

The abundance of mercury in the earth's crust is estimated to be 80 ppb (Green, 1959), and the abundance of mercury in soils is estimated to be about 100 ppb (A. P. Pierce and others, this report). Mercury in the atmosphere is derived from surface rocks and soils and from continuing hypogene and supergene processes.

Elemental mercury results from either process, and owing to its relatively high vapor pressure, it is released to the atmosphere. More mercury is found in air over mercury deposits than elsewhere, and the rate of release of mercury over the deposits is determined by barometric pressure and temperature. The data shown in table 28 indicate that anomalous concentrations of mercury are found in air over mineral deposits but that small amounts are found in air over nonmineralized areas. The data of figure 7 indicate a seasonal variation in the mercury content of air which may be the result of seasonal temperature variation. The data shown in figure 8 indicate that daily variations result from changes in barometric pressure. Lesser concentrations of mercury are found in air over the ocean; Williston (1968) found 0.6 to 0.7 ng/m³ of mercury 20 miles offshore over the Pacific Ocean, suggesting that the land surface is the principal source of mercury in the atmosphere.

CONCLUSIONS

Several tentative conclusions about mercury in the atmosphere can be drawn:

1. Mercury vapor is released to the atmosphere by evaporation from and by degassing of surface material.
2. Mercury content of air is highest over areas where the rocks are richest in mercury (2,000 to 20,000 ng/m³ at the surface and 24 to 192 ng/m³ at 100 ft).
3. The maximum content of mercury in air was found near midday; lesser amounts were found in the morning and evening; and minimum amounts were found near midnight.
4. The mercury content of ground surface air is considerably higher than that of air above the ground (108 to 20,000 ng/m³ at the Ord mine).
5. Background concentrations of mercury in air at 100 feet above ground in the Southwestern United States range from 3 to 9 ng/m³.

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ATMOSPHERIC AND FLUVIAL TRANSPORT OF MERCURY

By E. A. Jenne

Mercury is supplied to the environment from many sources. Near-surface mercury-bearing mineral deposits, industrial wastes and exhausts, and applications of agricultural chemicals serve locally to increase the mercury level of streams, lakes, and impoundments. Natural laws govern the rate and manner of movement of mercury.

ATMOSPHERIC TRANSPORT OF MERCURY

Mercury enters the atmosphere in both gaseous and particulate forms. The mobility of mercury is greatly enhanced by a property which is unique among the metals, namely the relatively high vapor pressure of the metallic state and, to a lesser extent, certain of its compounds. The vapor pressure is sufficiently high that air drying at 20°C for 2 days in a sealed box through which previously dried air was passed resulted in losses of 16, 24, 42, and 42 percent of the mercury originally present in minus 200 mesh fractions of four soils (Kokesy and others, 1967). These authors also note "the detectable mercury content of a sample originally containing 220 ppb (5 determinations) was increased by 25 percent when stored for 30 days at room temperature in the same box as a sample containing 8,000 ppb mercury."

The rate of vaporization of mercury and certain of its inorganic compounds decreases in the sequence Hg > $HgCl_2$ > HgCl > HgS > HgO according to the data of Kokesy and Bradshaw (1960). Vapor pressure of mercurial fungicides is much greater for the methyl and ethyl forms (0.8 to 28 times 10^{-3} mm (millimeter) mercury at 55°C) than phenyl forms (0.8 to 17 times 10^{-6} mm mercury at 55°C) (Phillips and others, 1959). Methylmercury chloride is the most volatile of the compounds tested[1] (23×10^{-3} mm mercury at 55°C). The methyl and ethyl forms tested, other than methylmercury chloride, have a volatility similar to metallic mercury (1.2 to 3.4 times 10^{-3} mm mercury (Phillips and others, 1959).

Gaseous and particulate mercury are commonly contained in the exhaust fumes from various industrial and smelting processes. Dust from sulfide-bearing mineral deposits may occasionally be a significant local source of mercury, inasmuch as "dust obtained during the treatment of tin ores" has been used for the industrial recovery of mercury (V. E. Polarkov, cited by Bergeev, 1961). Mercury may be vaporized directly from the land surface, particularly from mineralized areas, by radiant energy. The saturation level of mercury in air in equilibrium with metallic mercury, increases logarithmically with increasing temperature (Vaughn, 1967). Bergeev (1961) found the mercury content of soil air over a mercury ore deposit to be ≥ 100 ng/m^3, whereas the atmospheric air immediately over the deposit contained 10 to 20 ng/m^3. By comparison of these values with the value of 10^6 ng/m^3 for air saturated with metallic mercury vapor at 17°C (Vaughn, 1967), the soil air sampled by Bergeev would appear to have been undersaturated by a factor of about 10^2. The high degree of undersaturation of the soil air directly over a mercury deposit probably represents the faster rate of exchange of soil air with atmospheric air as compared to the rate of evaporation of mercury and its volatile compounds. McCarthy and others (1969) concluded that mercury in soil air samples was unrelated to the mercury content of the soil from which it was sampled, hence, most of the mercury in the soil air was assumed to come from greater depth. According to Williston (1964), the presence of a water table above mercury deposits does not greatly reduce the rate of mercury loss by vaporization.

Presumably, the microbial methylation of mercury (P. E. Greeson, this report) will increase the vapor phase loss of mercury. Although monomethyl mercury is the principal product of biological m th-

[1] Methylmercury chloride, mercuric (mix powder milk tale); ethoxyethyl mercuric chloride (tech.); methoxyethyl mercuric chloride (tech.); ethylmercury chloride, ethylmercuric hydroxide hydrochloride, methoxyethyl mercury chloride (tech.); ethoxyethyl mercuric chloride (tech.); mercuric chloride; ethylmercuric dicyandiamide (tech.); methylmercuric dicyandiamide; bis ethylmercury phosphate; ethylmercury acetate (mixed isomers); phenylmercuric acetate; phenylmercury oxinate; phenylmercury lactate; phenylmercury salicylanilide (tech.); phenylmercury 8-quinolinolate; phenylmercury chloride; bis phenylmercury methanedisalicylphenolate (tech.); phenylmercuric nitrate; phenylmercuric acetate; 8-(N-dimethylamino)-quinolate

viation (Jensen and Jernelöv, 1969), to the extent that the uncharged dimethyl mercury complexion is also formed, a net increase in volatility will result.

Little is known concerning the extent or nature of the reactions of gaseous mercury with earth materials although gaseous mercury readily forms amalgams with the noble metals platinum, gold, and silver. Ginsburg (1960, p. 104) and Kokesy and Bradshaw (1969) assumed that gaseous mercury is sorbed by organic matter and clays. If it is, then the amount of gaseous mercury that escapes from the land surface into the atmosphere is appreciably less than it would otherwise be. To the extent that this process occurs, the amount of mercury vapor in the atmosphere is being continually decreased by reaction with air-borne particulate matter and with the land surface. Mercury that enters the atmosphere is returned to the earth's surface. Some of the particulate atmospheric mercury returns to the earth in dry fallout, but most of the atmospheric mercury, both gaseous and particulate, returns to the earth in rainfall. Stock and Cucuel (1934) reported five rainwater samples whose mercury contents were only a few tenths of a part per billion above the background value of approximately 0.01 ppb. They also reported that the average of 12 samples, whose mercury content was significantly greater than the background value, was 0.2 ppb; the maximum value found was 0.43 ppb. The atmospheric mercury yield by rainfall was estimated by Andersson and Wiklander (1965), who reported 1.2 grams per hectare per year (0.48 gram per acre per year) in Sweden and noted that this amount is about the same as that used for seed dressing (fungicide). Near industrial areas, more mercury may possibly be deposited by dry fallout than by rainfall during dry seasons. Thus, Dams and others (1970) found 2½ times as much particulate mercury in the atmosphere in an industrial area of Chicago as in a rural area; that is, 1.8 versus 1.9 ng/m³.

FLUVIAL TRANSPORT OF MERCURY

The oxidation of mercury-bearing sulfide ores presumably results in the formation of both mercuric and mercurous ions. Mercurous chloride (Hg_2Cl_2) is only slightly soluble (0.002 g/l (gram per liter) or 2,000 ppb). It has a strong tendency to disproportionate according to the reaction $Hg_2^{++} \rightarrow Hg^0 + Hg^{++}$ under aqueous conditions (Sidgwick, 1950, p. 394). This reaction may be promoted by ultraviolet radiation (Sidgwick, 1950, p. 295). James (1962) suggested that the rather insoluble basic sulfate salt $Hg_3SO_4(OH)_2 \cdot H_2O$ is also likely to form as the result of oxidation of mercury-bearing sulfide ores. Mercuric chloride, $HgCl_2$, being highly soluble (66 g/l at 25° C), will be readily leached by rainfall and carried to streams by runoff, underflow, or ground water discharge. Rainfall-induced erosion and leaching also convey a part of the atmospheric mercury, previously returned to the land surface, to streams and other waters. Of course, a part of the atmospheric mercury is returned directly to water bodies by dry fallout and rainfall. According to Warren, Delavault, and Barakso (1966) the mercury content of soils varies appreciably in the areas studied by them. Soils completely unaffected by mineralization or local industrial contamination varied from 10 to 50 ppb of mercury. In contrast, soil within some hundreds of feet of mercury associated major base metal deposits run from 250 to 2,500 ppb of mercury. In the immediate area of mercury mineralization, soils commonly contained from 10,000 to 20,000 ppb but ranged from 1,000 to 50,000 ppb of mercury. They suggest that where the soil B or C horizons contain more mercury than the A horizon, which is commonly enriched by vegetative litter, it is probable that there is mineralization in the immediate vicinity. However, they note that anomalous clay or organic matter contents of the various horizons may alter this general rule.

Where streams have incised mercury-bearing deposits, both solute and particulate mercury are released directly to the fluvial environment. In places, thermal springs, nonthermal springs, and mine drainage contribute significant amounts of mercury to streams.

Quantitative data on the sorption and desorption of ionic mercury by earth materials were not found in the literature in the course of the preparation of this report. However, in common with other metals such as zinc and cadmium (Rankama and Sahama, 1950, p. 715; Goldschmidt, 1954, p. 275) or antimony (Kokesy and Bradshaw, 1969), mercury appears to be strongly sorbed by soils and sediments. Mercury must be fixed, that is, be desorbed very slowly, by soils and fluvial sediments. Otherwise, the high vapor pressures of free mercury and certain of its compounds as well as the solubility of the chlorides of mercury would preclude the notable enrichment of some soil horizons over mercury deposits and the very considerable increase in mercury concentration in fluvial sediments immediately below industrial outfalls that contain mercury

[1] Incorrectly cited by Rankama and Sahama (1950, p. 715) as 4 ppb.

wastes. Likewise, the affinity of certain soils for mercury is indicated by the failure of mercury applied as orchard sprays (phenylmercury acetate) over a period of several years to migrate below the surface 9 inches; the soil contained 500 or 1,100 ppb of mercury depending on the number of sprays applied (Ross and Stewart, 1962). A further indication of the tendency of mercury to be sorbed by solids is the marked loss of mercury from solution when unacidified water samples are stored in either polyethylene or glass containers. From 50 percent to 175 percent of the mercury lost from solution was recovered by acid washing the glass containers in which water samples were stored for only 2 weeks (Hinkle and Learned, 1969). It has been observed that the amount of mercury present in the surface horizon of five Swedish soils varied directly with the organic matter content (Andersson and Wiklander, 1965) and that both plankton and peat moss sorbed significant amounts of mercury from solution (Krauskopf, 1956). Mercury forms stable complexes with a number of different types of organic compounds found in natural waters, such as sulfur-containing proteins and humic materials. Some species of marine algae concentrate mercury from sea water to more than 100 times the sea water value of 0.03 ppb (Stock and Cuenod, 1951). Mercury is also concentrated to some degree in coal (Goldschmidt, 1954; and Michael Fleischer, this report) and notably in petroleum fluids (D. E. White and others, this report). Inasmuch as mercury forms many stable organo-metallic compounds including sulfur-containing proteins, probably a very significant part of the cationic mercury that has resided in natural fresh waters for times on the order of hours to days will be in some organic form. Furthermore, one may in some cases find a greater amount of mercury in the particulate fraction than in the solute fraction where the amount of suspended solids is relatively high and especially where the relative quantity of particulate organic matter is high relative to the soluble organic matter. Hinkle and Learned (1969) found from five to 25 times as much mercury in a 1 *N* hydrochloric acid extraction of the suspended sediment separated from some samples as was found in the filtrate.

The single analysis found of marine manganese nodules for mercury (J. P. Riley and P. Sinhaseng, cited by Mero, 1965, p. 181) yielded a value of 2,000 ppb, a concentration factor of 10^5 over the 0.03 ppb level in sea water. Likewise, manganese ores and "brown" iron ore are reported to contain as much as 1,000 ppb (A. A. Saukov, 1946, cited by Sergeev, 1961). In support of these observations are the finding of Krauskopf (1956) that initially divalent mercury was effectively sorbed by microcrystalline iron oxides. In solutions containing 50,000 ppb of Fe_2O_3 gel and initial mercury concentrations of 500 ppb, 90 to greater than 95 percent of the mercury was sorbed by the iron oxide within a few days. Montmorillonite was less effective as a sorbent (≈10 times more solids required to obtain similar sorption efficiency). A number of limonite samples from chalcopyrite deposits in the Southern Ural Mountains had an average mercury content of 18,000 ppb (Ginsburg, 1960, p. 101). The sorption efficiency ascribed to clays (Kukacy and Bradshaw, 1969) is very likely due to the nearly ubiquitous microcrystalline iron and, to a lesser extent, manganese oxide coatings present on the clays (Jenne, 1968; Andersson and Jenne, 1970). James (1962) has postulated the sorption of mercuric chloride anion complexes ($HgCl_3^-$, $HgCl_4^{--}$) by clays; sorption of molecular salts (Hg_2Cl_2, $HgCl_2$) is also a possibility. The hydrous oxides of iron and manganese provide the most likely sites for both anionic and molecular salt sorption by earth materials.

Less rapid reactions that may remove mercury (Hg^{++} radius = 1.10 angstroms) from waters and soils solutions are the possible isomorphous substitution for barium (Ba^{++} radius = 1.34 angstroms) and, to a lesser extent, for calcium (Ca^{++} radius = 0.99 angstrom). However, the much greater electronegativity of mercury (1.9) than of calcium (1.10) and the fact that the ionic radius of divalent mercury is more than 10 percent smaller than the ionic radius of barium will certainly limit its solid solution for calcium and barium (Ringwood, 1955). Nonetheless, in districts that contain metallic mercury, barium sulfate (barite) may contain from 20,000 to 100,000 ppb mercury (A. A. Saukov, 1946, cited by Sergeev, 1961). Similar results were obtained by Vershkovskaia (1956, cited by Ginsburg, 1960, p. 19).

Little information is available on the cation exchange properties of mercury. Ginsburg (1960, p. 155) stated that "Divalent ions form the following series, in reference to their uptake by montmorillonite from aqueous solutions: Pb > Cu > Ca > Ba > Mg > Hg, and in reference to the facility of the replacement, Mg > Ba > Ca > Cu > Pb. The energy of adsorption series of heavy metals by kaolinite are as follows: Hg > Cu > Pb; the calcium replacement series Pb > Cu > Hg." Thus, it appears that the sorption capacity of this kaolinite for mercury is low, but that mercury which is sorbed is held strongly.

A regular decrease in mercury down the Paglia River (Italy) below a mercury anomaly was observed by Dall'Aglio (1968). The mercury concentration in the stream water decreased from a high of 180 ppb to a low of 0.01 ppb 50 to 60 kilometers downstream. (It is not clear from the paper whether these analyses are on filtered or unfiltered samples; presumably they were filtered). Wisconsin River sediment contained 560,000 ppb at a chemical company outfall but only 50,000 ppb 4 miles downstream (Chemical and Engineering News, 1970). The mercury concentration in the sediment had decreased to 100 ppb 21.1 miles downstream (Francis H. Schraufnagel, oral commun., July 30, 1970). The downstream decrease in the amount of mercury in the sediment is indicative of the rapid downstream decrease in mercury concentration. Concerning possible seasonal variations, Heide, Lerz, and Böhm (1957) concluded that such variations did not occur in the mercury content of the Saale River (Germany) although they reported a minimum value of 0.068 ppb and a maximum value of 0.141 ppb of mercury at one sampling station in the course of a year. A progressive increase in downstream mercury concentration in the Saale River due presumably to industrial pollution is indicated by their data.

EXPERIMENTAL DATA

Recent experimental data indicate that the sorption of mercury by membrane filters is minimal and that mercury sorption by peat moss, microcrystalline oxides, and soils is rapid (V. C. Kennedy, unpub. data, 1970). Solutions containing 1 and 10 ppb of mercury (originally divalent) were made up in tap water prefiltered through a 0.1 micron membrane filter. From 1 to 7 percent of the mercury in 50 ml (milliliters) of these solutions was retained by 0.45-micron 2-inch cellulose acetate membrane filters in a single pass. This was true for both pH 6 and 8 solutions. Sorption of mercury by three soils, by a microcrystalline manganese oxide, and by peat moss was rapid. From half to nearly all the mercury in 50 ml of a 10 ppb solution of pH 6 was sorbed within 1 hour by 1-gram samples. After 24 hours, all the samples had sorbed more than three-fourth's of the added mercury.

The amount of mercury desorbed in 1 hour from the manganese oxide, from the 24-hour set of samples, by filtered tap water and subsequently by one-half normal sodium chloride (to approximate estuary salinity) was between 10 and 20 percent and 60 to 40 percent, respectively. The remainder of the 24-hour set of samples desorbed from less than 1 to 5 percent of the mercury originally sorbed, using filtered tap water. Subsequent desorption in one-half normal sodium chloride in general removed slightly less mercury than was desorbed by tap water. A similar amount of mercury was desorbed from the manganese oxide from both the 1-hour and the 24-hour sorption sets. However, a slightly lesser percentage of the mercury originally sorbed was desorbed from the other samples which were exposed to mercury-containing solutions for 24 hours. From 2 to 7 percent was desorbed in tap water and 1 to 2 percent in one-half normal sodium chloride.

Thus, mercury at trace concentrations is rapidly taken up by microcrystalline oxides, peat moss, and soils. Most of the mercury was held irreversibly against filtered tap water and one-half normal sodium chloride. However, it is not known to what extent the uptake by these earth-material samples is due to sorption of cationic mercury and to what extent the uptake may be due to a reduction to metallic mercury. The Eh-pH diagrams of Symons (1966) and the discussion of J. D. Hem (this report) indicate that metallic mercury is the stable form in most natural fresh waters. In very well oxygenated acid to neutral waters the mercurous ion may be the stable ion whereas under alkaline conditions the mercuric oxide, montroydite, may be the stable phase.

FATE OF MERCURY INTRODUCED INTO ENVIRONMENT

Mercury is being continuously removed from the atmosphere and deposited on the earth's surface by dry fallout and by rainfall. Solute mercury introduced into streams is quickly transformed to the particulate form by reduction to metallic mercury, by sorption on to inorganic sorbates, by co-precipitation with nonviable particulate organics, and by sorption and ingestion by viable biota. The available evidence (Heide and others, 1957; Dall'Aglio, 1968; V. C. Kennedy, unpub. data, 1970) is that stream sediments and related fine-grained materials remove a high percentage of any slugs of mercury introduced into streams, within a distance of a few to several miles, depending on the existing redox potentials, the amount of suspended sediment, stream discharge, and the mineralogical-chemical nature of the sediment.

When a mercury pollution source is eliminated, mercury will be slowly released from bed sediment to the stream water over a period of time (possibly months) until a steady state condition is reached.

The complexing of mercury by soluble organics

will greatly increase its mobility as will the formation of strong inorganic complex ions. Considering the known ability of natural soluble organics to extract trace metals from soils and sediments, it is likely that to a first approximation the mobility of mercury in natural waters will be dependent upon the amount and chemical nature of the soluble organics present. Thus, mercury may have greater mobility in waters containing large amounts of dissolved organics. In the case of ground waters, the mercury concentration has been found to be directly related to their bicarbonate content (Karasik and others, 1965).

The quantity of sediment in transport is the second most important factor in determining the downstream movement of mercury. For example, Hinkle and Learned (1969) found from five to 25 times as much mercury in the suspended sediment as in the filtered water.

Organic pollution of natural waters, whether from natural or manmade sources, frequently causes reducing conditions to develop on the streambed. The occurrence of reducing conditions will cause the partial release of sorbed mercury due to dissolution of manganese and iron oxides present in the sediment. On the one hand, this will have the effect of enhancing mercury mobility by increasing the amount of mercury available for complexing by organics at the expense of mercury sorbed by the inorganic sediments. On the other hand, it is likely that under such reducing conditions a significant part of the mercury present will be reduced to the metallic state. This will decrease its mobility to the extent that the metallic mercury amalgamates with iron oxides or falls to the bed as droplets. (However, Fedorchuk (1961) notes that mercury is not concentrated in the heavy mineral fraction of shales.) The solubility of metallic mercury, in the presence of 5 to 10 ppb of chloride and under conditions where the mercurous ion is stable, is generally less than 2 ppb (J. D. Hem, this report). However, the total solubility of both dissociated and undissociated species is from 20 to 30 ppb (Sidgwick, 1950, p. 987; Parlund and Archinard, 1952). Thus, mercury can be expected to be released to the stream water rather slowly. The apparent ease of microbial transformation of inorganic mercury in bed sediments to the highly soluble methylmercury form (P. F. Gleason, this report) will noticeably increase mercury mobility. This transformation can be rather rapid, near steady state conditions being reached in a few days in batch tests (Jensen and Jernelöv, 1969). The release of sulfides to or production of sulfide in the stream, as a result of reducing conditions, may markedly affect the mobility of mercury. The precipitation of the rather insoluble mercuric sulfide, HgS (1.30×10^{-4} g/l, Sidgwick, 1950, p. 995), will tend to concentrate mercury in the sediment. In those unusual instances wherein alkaline reducing conditions exist, and hence greater sulfide concentrations occur, the formation of the rather soluble HgS_2^{--} ion may facilitate mercury transport. Although mercuric mercury is generally unstable with respect to metallic mercury in stream waters (Symons, 1969), mercuric sulfide is formed by the reaction $Hg + S^{--} + Hg^{++} \rightarrow HgS$ (Sidgwick, 1950, p. 995).

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ANALYTICAL METHODS FOR DETERMINATION OF MERCURY IN ROCKS AND SOILS

By F. N. Ward

The mercury content of most uncontaminated solid earth materials is between 10 ppb and 500 ppb, and for water resources, generally is less than 0.1 ppb, as is shown by data elsewhere in this report. Hence, to be useful, any analytical method must be at least sensitive enough to detect as little as 10^{-8} gram and in some analyses one or two orders of magnitude less. With the exceptions of the techniques described by Ward and Bailey (1969) and by L. L. Thatcher (written commun., 1970), both discussed below, all methods mentioned in this article measure *only* inorganically-bound mercury. Using the best applicable methods, analytical limitations of the methods are 10 ppb for rock and soils and 0.1 ppb for aqueous solutions if 100 ml (milliliters) of sample is used. An exception to this statement is the neutron activation method which may reach 0.05 ppb for water and sediment samples.

The requirements of sensitivity limit the number of techniques that appear useful for determining trace amounts of mercury in soils and rocks. (Although not rigorously defined, trace amounts may be considered as those occurring at 0.01 percent (100,000 ppb) or less.) Among the applicable techniques, including kinds of separations as well as final measurements, are those based on molecular and atomic absorption, molecular and atomic emission, catalysis, nephelometry, polarography, and activation to produce measurable decay products. Several analytical methods for determining trace amounts of mercury in geologic materials based on some of these techniques are discussed below. Gravimetric and volumetric methods are not generally applicable, but under certain conditions large samples can be taken and the separated mercury measured by weighing or titrating with thiocyanate in the presence of iron alum to a persistent pink color (Hillebrand and Lundell, 1953). An old gravimetric method (Eschka, 1872, quoted in Hillebrand and Lundell, 1953) is discussed below.

The literature on analytical methods for determining mercury in soils and rocks is voluminous, especially when one considers that most of this literature covers less than a half century. Interests of agricultural chemists in the effects of trace elements in agriculture and of a few scientists like Goldschmidt and the Noddacks in trying out a new technique—the spectrograph utilizing emission phenomena—account in part for the literature becoming so large in such a short time. Fischer's (1925) research on the newly discovered large molecular compounds, such as dithizone, that were capable of reacting with 10^{-8} gram and less of certain metals (especially mercury) to produce highly colored products triggered the development of trace analytical methods.

Because of the vast literature available no claim is made of complete coverage herein, and the mention of a particular method to the exclusion of others is only for illustration and with no intended bias. Emphasis here is on procedures used by the U.S. Geological Survey because of the author's greater experience with them.

Molecular absorption—absorptiometric, spectrophotometric, colorimetric—methods depend on the reaction of mercury under special conditions such as pH, etc., with high molecular weight compounds—usually organic—to form a species that uniquely absorbs certain light frequencies in the visible or ultraviolet range. The amount of absorption can be measured instrumentally or visually and then related to the initial concentration of mercury in a homogeneous, isotropic medium; most often it is an organic solvent. Immiscible organic solvents are especially useful for enriching the species to a threshold level and for removing it from other compounds so as to inhibit or prevent interfering side reactions.

Dithizone is one of the most common organic reagents that forms a highly colored and extractable species with Hg^{++}. The molar absorptivity of Hg^{++} dithizonate is about 70,000; that is, as little

as 0.019 microgram Hg per square centimeter gives a measurable absorbance of 0.001 to 0.005 (unit difference in percent transmission as usually measured instrumentally). Differences of such magnitude are easily measured, and the dithizone procedure therefore is applicable to mercury concentrations found in soils and rocks. The dithizone reaction was the basis of the first practicable field method for determining traces of mercury in such materials (Ward and Bailey, 1960). Briefly, the procedure involved treatment of a finely powdered sample with sulfuric and hydrobromic acid and bromine in a test tube. The acidity of the sample solution was adjusted to pH 4 and treated with dithizone in n-hexane. Separation of the organic from the aqueous solution and subsequent removal of unreacted dithizone left an amber-colored solution of mercuric dithizonate whose intensity was measured visually against that of standard solutions.

The phenomenal growth of atomic absorption methods following the classic paper by Walsh (1955) tends to hide the fact that atomic absorption determinations of mercury were made by nontechnically oriented prospectors in the latter part of the 19th century. Mercury is unique with respect to its high volatility and resulting large number of ground state atoms in the vapor. Such atoms absorb resonant frequencies of incident energy, and the amount of absorbed energy is proportional to the concentration of mercury.

Instrumentation useful for determining many elements became commercially available in the early 1960's and since then even more chemical elements can be determined by atomic absorption. Sample introduction is done in two different ways. In one technique the sample is prepared in a solution, which is nebulized in the acetylene-air flame that is positioned in the path of incident energy. In a second technique, which is unique to mercury, the sample is volatilized from a soil or rock sample to heat or from a solution prepared from the sample, and the resulting vapor is introduced into the path of incident energy. The first technique is used by Tindall (1967) and variants of the second are used by Brandenberger and Bader (1967) and Hatch and Ott (1968). Sensitivities of the second technique are of the order of 0.1 to 0.2 nanogram of mercury; if the starting solution contains all the mercury extracted from a 1-gram sample, an analyst could measure as little as 10^{-7} gram mercury in geologic materials. This is equivalent to 0.1 ppb.

In the U.S. Geological Survey laboratories, mercury in soils and rocks is measured by an instrumental atomic absorption method described by Vaughn and McCarthy (1964) and Vaughn (1967). The sample is heated to about 500° C in an rf (radio frequency) field to drive off mercury and particulate and vapor oxidation products of any organic material. The mercury is trapped on gold or silver leaf, and the other evolved products are shunted through a bypass and out of the system (diagramed by Vaughn, 1967). Then the rf field is changed so as to heat the gold or silver leaf, and the two-way stopcock is rotated in order to direct the mercury into the long measuring chamber, which has an ultraviolet lamp near one end and a photocell detector at the other. The ground state atoms in the mercury vapor attenuate the light from the ultraviolet lamp, thereby decreasing the current output of the photocell. The decrease is amplified in a differential amplifier causing a meter deflection that is proportional to the concentration of mercury. Under routine conditions the sensitivity achieved is about 1 ppb, which is quite adequate for signaling anomalous concentrations in soils and rocks.

Mercury in aqueous solutions is determined by amalgamation on a silver screen and subsequently heating the dried screen in a rf heating coil. The released mercury vapor is measured in a mercury-vapor absorption detector. The technique is described by Hinkle and Learned (1969).

A similar method for sediment free water samples (Fishman, 1970) follows. The water samples are filtered through 0.45 micron membrane filters immediately after collection and acidified with 1.5 ml of concentrated nitric acid per liter of sample to stabilize the mercury and to minimize loss by sorption on container walls. Mercury is collected from the acidified water sample by amalgamation on a silver wire. The silver wire is electrically heated in an absorption cell placed in the light beam of an atomic absorption spectrophotometer. The mercury vapors are drawn through the cell with a water aspirator and the absorption is plotted on a recorder. Samples containing between 0.1 and 1.5 ppb of mercury can be analyzed directly; samples containing more than 1.5 ppb must first be diluted.

Much of the data given in this report, and especially those used to produce the statistics shown in A. P. Pierce and others (this report) were obtained on atomic absorption units similar to those just described.

Analytical methods based on optical emission spectrography are seldom used in the U.S. Geological Survey when many geologic samples must be an-

alyzed and time is short. Without specialized techniques to enrich the mercury content of the sample or to maintain the excited mercury atoms in an arc column for several seconds, the overall sensitivity of spectrographic methods is inadequate. Several Russian workers have exercised the patience and skill needed to utilize the potential of optical emission spectrography in measuring trace amounts of mercury in soils and rocks; hence the method should not be underestimated. For the most part, however, the availability of other procedures that achieve greater sensitivity with less effort precludes any large-scale and in-depth investigations of optical emission spectrography to determine mercury in ordinary materials such as soils, rocks, and vegetation.

Analytical methods based on catalysis are potentially applicable to the determination of trace amounts of mercury in soils and rocks. One such method used by the Geological Survey is described by Hinkle, Leong, and Ward (1966). This procedure is based on the catalytic effect of mercury on the reaction of potassium ferrocyanide with nitrosodimethylaniline to give a violet-colored compound, whose intensity is proportional to the mercury concentration. The color can be measured instrumentally or visually. As little as 3×10^{-9} gram (10 ppb) of mercury is readily measured, and starting with a 1-gram sample, the analyst can measure concentrations as little as 50 ppb.

Until recently, gravimetric methods of chemical analysis have not been useful in determining constituents occurring in amounts of 0.01 percent (100,000 ppb) or less. Owing to recent improvements in the sensitivity of analytical balances and especially the improvements that permit accurate weighing to a microgram or less, gravimetric methods should be evaluated, and the Eschka gravimetric method for assaying mercury in soils and rocks shows new promise.

The Eschka method consists of heating a sample in the presence of copper (CuO) oxide and lime in a closed system and amalgamating the volatilized mercury onto gold foil. With the improved analytical balances the amalgamated mercury can be measured by weight, and the increase resulting from amalgamation is proportional to the mercury content of the sample.

Mass spectrometry has quite recently been used for determining trace amounts of mercury in geologic materials. The method is sensitive and fast, especially when directly linked to computer facilities, but the large initial costs as well as the need of skilled operators limit its application.

Activation methods for determining trace amounts of mercury have been described by several authors including Brune (1968) and Dams and others (1970). The sensitivities achieved by these authors range from 0.1 nanograms to 80 nanograms depending on type of sample, irradiation time, and chemical treatment. Measurement of the gamma (γ) radiation of Hg^{197} (65-hour half life) after irradiation for 70 hours with a flux of 10^{12} nanograms per square centimeter per second yields an absolute sensitivity of about 5 nanograms in a nondestructive procedure devised by L. H. Ekvall and T. Westermark (written commun., 1965). A sensitivity one order of magnitude less was achieved by Bjurstrand (1961) in a destructive technique.

According to L. L. Thatcher (written commun., 1970) neutron activation analysis is now being used to determine mercury concentrations in water and sediments down to 0.05 ppb. Two methods have been developed: (1) A reference method which is very specific for mercury and is capable of extracting mercury from the stable complexes with which it may be associated in water, and (2) a more general method for toxic heavy metals including mercury. In the reference method, 20 milliliters of water sample are irradiated in a sealed quartz vial at 1 megawatt for 4 hours. The mercury isotopes Hg^{203m} (24-hour half life) and Hg^{197} (65-hour half life) are generated. After irradiation the mercury isotopes are isolated by performing a carrier precipitation with added mercury salt followed by stannous chloride. The latter reduces the mercury and radio-mercury compounds to the free metal including any radio-mercury that may be tied up as a stable complex. The activity of Hg^{197} is counted in a coaxial Ge(Li) detector at 77 kilo electron volts. The combination of chemical isolation of radio-mercury and photon spectrum characterization provides very specific identification of mercury. Sensitivity of the method may be extended down beyond 0.05 ppb by taking a larger water sample for the irradiation and (or) by increasing the irradiation time.

The more general toxic heavy metal determination is carried out by stripping the heavy metals from a 10 ml water sample by sulfide precipitation using lead sulfide as carrier. The mixed sulfide precipitate is activated (lead does not activate) in polyethylene or quartz as above. The lead sulfide protects the mercury from significant volatilization during irradiation and also minimizes sorption loss to the polyethylene. After irradiation, the photon spectrum of the sulfides is scanned to identify the characteristic photo peaks of mercury, copper, chro-

mium, cadmium, cobalt, and arsenic and to quantify these heavy metals. The success of the method depends on the ability to make a lead sulfide precipitate of sufficiently high purity. This has not proved to be a significant problem but reagent blanks are always run as a precaution.

The reference method can be applied to the determination of mercury in waterborne materials, such as sediment and biota, by dissolving the irradiated material in hydrofluoric or oxidizing acids and following through with the carrier precipitation.

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TABLES 1-28

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TABLE 1.—[illegible]

Sample	[illegible]	Unit	Method
[illegible] U. S. Rhode Island	[illegible]	[illegible]	[illegible]
[illegible] W. S. Virginia	[illegible]	[illegible]	[illegible]
Granodiorite PHP 1, Colorado	[illegible]	[illegible]	[illegible]
Andesite AHV 1, Oregon	[illegible]	[illegible]	[illegible]
Basalt BCR 1, Washington	[illegible]	[illegible]	[illegible]
Peridotite PCC 1, California	[illegible]	[illegible]	[illegible]
Dunite DTS 1, Washington	[illegible]	[illegible]	[illegible]

[illegible] It has been suggested that some of the samples analyzed had been contaminated by mercury during long storage in the laboratory.

TABLE 2.—*Analyses for mercury, in parts per billion, of basalts, gabbros, diabases, andesites, diorites, and hyperites* [illegible]

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Basalt PCR 1, Washington	1	[illegible]	[illegible]	[illegible]	[illegible]
Diabase W-1, Virginia	1	[illegible]	[illegible]	[illegible]	[illegible]
Three Hawaii, Two Antarctica, Ireland, Hawaii, and Tasmania	5	[illegible]	[illegible]	[illegible]	[illegible]
Basalts, oceanic sediments near Iceland		100	600	[illegible]	[illegible]
Gabbro, Quebec	1	[illegible]	[illegible]	[illegible]	[illegible]
Composite I gabbros, Germany	[illegible]	[illegible]	[illegible]	100	[illegible]
Composite II gabbros, Germany	[illegible]	[illegible]	[illegible]	80	[illegible]
Gabbros, Yakutia	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Gabbros, northern Caucasus	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Gabbros	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Basalt, Germany	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 5.—*Analyses for mercury, in parts per billion, of basalts, gabbros, diabases, andesites, diorites, and tiperites*—Continued

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Basalt, Yakutia	1	0	40	20	Nekrasov and Timofeeva (1983).
Basalt, Kamchatka and Kuriles	65	20	100	47	Osserova and Ulyanova (1985).
Basalts, andesites, Mendeleev Volcano, Kuriles		100	130		Osserov and others (1980).
Lavas, central Kamchatka				100	Aidin'yan and Osserova (1984).
Lavas, eastern Kamchatka				410	Do.
Gramophyre, associated with dolerite, Tasmania	1			38	Ehmann and Lovering (1967).
Andesite, ADV 1, Oregon	1	4	18	17	Five labs.
Andesites, Kamchatka and Kuriles	200	60	1000	15	Osserova and Ulyanova (1985).
Trachytes, northern Caucasus	5	60	1000	130	Afanas'ev and Aidin'yan (1981).
Trachytic tuffs, northern Caucasus	15	60	1200	100	Do.
Eruptive breccia, northern Caucasus	1			500	Do.
Keratophyres, northern Caucasus	1	30	200	100	Do.
Diorites, Kamchatka	5	20	750	83	Osserova and Ulyanova (1985).
Diorites, Yakutia	9	50	70	60	Nekrasov and Timofeeva (1983).
Quartzites, Yakutia	1	13	400	10	Do.
Quartzites, northern Caucasus	1	10	50	90	Afanas'ev and Aidin'yan (1981).
Aphlimbites, northern Caucasus	1	40	80	65	Do.

TABLE 6.—*Determinations of mercury, in parts per billion, in granitic rocks*

[N.f., not found. Compare with table 8]

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Granite G-1, Rhode Island	1	70	240	150	Seven labs.
Granite G-2, Rhode Island	1	30	100	53	Six labs.
Granodiorite GSP-1, Colorado	1	15	41	28	Five labs.
Composite 14 German granites	1			100	Stark and Clarke (1984a).
Composite 14 German granites	1			100	Treuer (1949).
Granite, Karelia	84	10	75	30	Aidin'yan, Tsvetaeb, and Belyaykova (1984).
Granites, diorites, granodiorites, Pedablastan					Aidin'yan, Mogarovskii, and Mel'nichenko (1985).
Granitic rocks, Yenisei Range	65	5	180	25	Osserova and Yudelson (1979).
Granites, Yakutia	25	N.f.	50	20	Nekrasov and Timofeeva (1983).
Diorites, granodiorites, Yakutia	20	5	40	15	Do.
Diorites porphyrites, Yakutia	5	5	30	5	Do.
Granites and diorites	15	100	400	100	Osserova (1984).
Granites, northern Caucasus	1	100	300	100	Afanas'ev and Aidin'yan (1981).
Extrusive granitoids, northern Caucasus	1	100	300	150	Do.
Quartz porphyry, northern Caucasus	1	80	150	110	Do.
Porphyry, northern Caucasus	1	80	400	150	Do.

TABLE 7.—*Determinations of mercury, in parts per billion, in ultramafic and deep-seated igneous rocks*

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Peridotite PCC 1, California	1	1	11	5	Five labs.
Dunite DTS 1, Washington	1	<50	500	140	Do.
Serpentinites				100	Osserova (1984).
Kimberlite, South Africa				300	Ehmann and Lovering (1967).
Eclogite inclusion in kimberlite, South Africa				910	Do.
Garnet peridotite in kimberlite, South Africa				740	Do.
Eclogite inclusion in pipe, Australia				1,400	Do.
Granulite inclusion in pipe, Australia				1,300	Do.

TABLE 5.—*Determinations of mercury, in parts per billion, in alkalic rocks*

[Compare sub table 6]

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Average for four granosyenite porphyries, Caucasus, ca. Ybs. 2000, 3000		50	80,000	10 to 5,000	Abuov, Divakov, and Rad'ko (1965).
Nepheline syenites, etc., Lovozero massif, Kola Peninsula, U.S.S.R.	840	140	580	275	Aidin'yan, Shilin, and Unanova (1966).
Nepheline syenites, etc., Khibiny massif, Kola Peninsula, U.S.S.R.	170	30	4,000	540	Aidin'yan, Shilin, and Belavskaya (1963).
Nepheline syenites	72	60	300	200	Osseyva (1962).

TABLE 6.—*Determinations of mercury, in parts per billion, in igneous rocks of areas of very high content, mainly from the Crimea and Donets Basin, U.S.S.R.*

[Tr., trace]

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Diabase, Crimea	63	Tr.	500,000	17,000	Bulkin (1962).
Gabbro, Crimea	3	500	5,000	1,700	Do.
Basalts, Donets Basin	6	400	1,500	925	Butsulinov and Korchemagin (1966).
Trachyandesites, Donets Basin	1	600	540	570	Do.
Andesite basalts, Donets Basin	1	600	400	500	Do.
Camptonites, Donets Basin	15	80	550	300	Do.
Do.		4,000	7,000		Dvornikov and Kitchenko (1964).
Basalt, andesite, Viet Nam	1			6,000	Aidin'yan, Frantsiff, and Belavskaya (1964).
Andesites, Donets Basin	5	10,000	80,000		Dvornikov and Kitchenko (1964).
Dacite, Crimea	9	Tr.	21,000	2,100	Bulkin (1962).
Keratophyres, Crimea	7	Tr.	5,000	2,100	Do.
Granodiorites, Crimea	3	Tr.	1,000		Do.
Porphyrs, Crimea	15	Tr.	5,000	700	Do.
Plagiogranite, Donets Basin		4,000	7,000		Dvornikov and Kitchenko (1964).
Plagiosyenites, Donets Basin	6	500	600	550	Butsulinov and Korchemagin (1966).
Granite, Donets Basin	1	500		500	Do.
Monzonites, Donets Basin	3	400	940	700	Do.
Pyroxenites, Donets Basin	1	100	500	450	Do.
Shonkinites, Donets Basin	1	900	720	820	Do.
Nepheline syenites, Donets Basin	11	100	2,000	1,300	Do.

TABLE 7.—*Determinations of mercury, in parts per billion, in metamorphic rocks*

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Quartzites, Valdai Series, Russian platform	9	30	60	37	Osseyva and Aidin'yan (1966a, 1966b).
Paragneisses, Valdai Series, Russian platform	3	30	100	51	Do.
Granitic, Valdai Series, Russian platform	7	60	95	71	Do.
Orthoamphibolites, Valdai Series, Russian platform	5	60	70	61	Do.
Phyllites and schists, Ishyeh zone	190	7	28	15	Do.
Amphibolite, Quebec	1			15	Jovanovic and Reed (1966).
Pelitic schists, Vermont	13	0.3	2,500	660	Do.
Pelitic schists, Vermont (omitting highest)	13	0.3	120	60	Do.
Schists and hornfels, Khibiny massif, Kola Peninsula (country rocks of alkalic massif)	10	70	600	307	Aidin'yan, Shilin, and Belavskaya (1963).
Schist, northern Caucasus	1			60	Afanas'ev and Aidin'yan (1961).

TABLE 8.—*Analyses for mercury, in parts per billion, in limestones*

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Germany	1	25	200	43	Stock and Cucuel (1934a).
Nineteen Composites, Russian platform	19	25	200	60	Heide and Hohm (1957).
Argillaceous marls, Caucasus, Background = 50		10	5,000	61	Abuev, Divakov, and Radbil (1965).
Limestones, Crimean highlands	6	100	5,000	1,000	Rubkin (1962).
Marls, Crimean highlands	3	500	2,000	1,333	Do.
Donets Basin	911	100	10,000	900	Karasik and Goncharov (1964).
Kerch-Taman area, near mud volcanoes		3,000	5,000		Ershov and Morozov (1958).
Limestones and dolomites, southern Ferghana	27	20	150	75	Nikiforov, Aidin'yan, and Kuznetsh (1966).
Northeast Yakutia	26	2.5	70	16	Nekrasov and Timofeyev (1963).
Kazakhstan	600			<50	Fursov, as quoted by Ostrova and Aidin'yan (1966).
Marble, Viet Nam	1			500	Aidin'yan, Troitskii, and Belavskaya (1964).

TABLE 9.—*Analyses for mercury, in parts per billion, in sandstones*

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Composite of 24	2	25	40	33	Stock and Cucuel (1934a).
Sandstones, midstones, Russian platform	45	0	95	100	Preuss (1949).
Effusive sedimentary, Kamchatka	0			37	Ostrova and Aidin'yan (1966b).
Kazakhstan	600			50	Do.
					Fursov, quoted by Ostrova and Aidin'yan (1966b).
Northeast Yakutia	9	<2	50	12	Nekrasov and Timofeyev (1963).
Sandstones, Crimean highlands	83	100	11,000	2,700	Rubkin (1962).
Conglomerates, Crimean highlands	10	100	1,000	2,100	Do.
Donets Basin		<50	1,000	300	Dvornikov and Kitchenko (1964).
Donets Basin	77	<100	1,000	470	Karasik and Goncharov (1964).
Donets Basin, contact with dike	1			600	Bogushevov and Korchemagin (1966).
Donets Basin, from mercury deposit		1,000	10,000	6,000	Rod'shakov (1961).
Sandstones with limestones, southern Ferghana		1,000	10,000		Kurmanaliev (1967).
Viet Nam	4	200	1,000	600	Aidin'yan, Troitskii, and Belavskaya (1964).

TABLE 10.—*Analyses for mercury, in parts per billion, in shales and clays*

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Composite 18 German shales	1			400	Preuss (1949).
Composite 38 German shales	1			510	Stock and Cucuel (1934a).
Shales	3	100	400	183	Do.
Marly clays	3	100	300	166	Heide and Hohm (1957).
Clays, Russian platform	58	0	150	35	Ostrova and Aidin'yan (1966b).
Shales, northeast Yakutia	9	15	80	40	Nekrasov and Timofeyev (1963).
Shales, sandstones, southern Ferghana	28	20	150	70	Nikiforov, Aidin'yan and Kuznetsh (1966).
Shales, Komi A.S.S.R	36	12	350		Zav'yalov and Mal'tseva, quoted by Ostrova and Aidin'yan (1966b).
Argillites, sedimentary volcanic, Kamchatka	11			85	Nikiforov, Aidin'yan, and Kuznetsh (1966).
Alfuramping shale, Alaska	2	600	2,000		Dannell, Talbot, and Tourtelot (1967).
Oil shales, Baltic region	16	170	1,500		Ostrova and Aidin'yan (1966b).
Oil shales, Povolzhe region	17	300	1,000	410	Do.
Oil shales, Tula region	3	50	100	75	Do.
Silurian shales outside ore region		<100	200		Ostrova (1962).
Silurian shales within ore region		100	>5000		Do.
Shales, Crimean highlands	44	<100	10,000	3,000	Rubkin (1962).
Shales, Donets Basin	6	<50	50	50	Dvornikov and Kitchenko (1964).
Shales, Donets Basin, contact with dikes	8	<200	500	150	Bogushevov and Korchemagin (1966).
Shales, Donets Basin	55	<100	5,000	600	Karasik and Goncharov (1964).
Shales, Donets Basin, from mercury deposit		1,000	60,000		Rod'shakov (1961).
Clays, Kerch Peninsula		<100	1,000	600	Morozov (1965).
Clays, Viet Nam	4	100	550	270	Aidin'yan, Troitskii, and Belavskaya (1964).

TABLE 11.—*Analyses for mercury, in parts per billion, in miscellaneous sedimentary rocks*

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Flysch, not specified	11			50	Demidova, quoted by Ozerova and Aidin'yan (1968b).
Greece: Attica, not specified	9	40	160		Sherbatian, quoted by Ozerova and Aidin'yan (1968b).
Kerch-Taman area, near mud volcanoes		500	2,500		Karpuk and Murenov (1966).
Kerch-Taman area, away from mud volcanoes		100	800	540	Do.
Caucasus, Transcaucasia:		70	2,000		Shabalin and Sobolyeva (1967).
Black salt, anhydrite, gypsum, Donets Basin	31	<100	1,000	700	Karpuk and Gurevich (1967).
Phosphorites	30	30	500	70	Ozerova and Aidin'yan (1968a, 1968b).
Iron-rich laterites, Viet Nam		1,000	2,700		Do.
Manganese ores, Nikopol				2,000	Do.
Manganese ores, Chiatura		500	530		Do.
Manganese ores, Mangyshlak		80	87		Do.
Bauxites	4	150	600	400	Do.

TABLE 12.—*Analyses for mercury, in parts per billion, in oceanic and terrestrial sediments*

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Red clay, Atlantic	4	500	1,500	1,000	Aidin'yan, Ozerova, and Ilin [1968].
Red clay, Pacific	3	100	300	200	Do.
Red clay, Black Sea	3	600	2,000	1,000	Do.
Foraminiferal ooze, Atlantic	3	80	300	170	Do.
Foraminiferal ooze, Pacific	1			50	Do.
Foraminiferal ooze, Indian	3	70	150	110	Do.
Terrigenous ooze, Atlantic	3	80	530	315	Do.
Terrigenous ooze, Indian	1			70	Do.
Diatomaceous ooze, Pacific	3	60	100	80	Do.
Diatomaceous ooze, Indian	3			600	Do.
East Pacific		<1	1,400		Bostrom and Fisher (1969).
Coral sediments	5	1,400	2,000		Landstrom, Ramaekh, and Wenner (1969).
Carbonate sediments	3	100	810		Do.
Manganese nodules, Atlantic	3	<1	810		Harriss (1968).
Manganese nodules, Pacific	3	<1	970		Do.
Manganese nodules, Indian	4	<1	3		Do.
Manganese nodules, Atlantic				2,000	Ozerova and Aidin'yan (1968b).
Manganese nodules, Pacific		100	150		Do.

[In a carbonate-free basis]

TABLE 13.—*Analyses of soils for mercury, in parts per billion*

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Muck soils, California		40	40		Williston (1968).
Soils, Franciscan Formation, California		100	600		Do.
Soils, unmineralized areas, California		40	60		Friedrich and Hawkes (1966).
Unmineralized areas, British Columbia		10	50		Warren, Delavault, and Barakso (1966).
Near mineralization, British Columbia		50	5,000		Do.
Very near mineralization, British Columbia		250	2,000		Do.
Soils, Germany		40	200		Stock and Cucuel (1934a).
Taiga soils, Sweden	274			60	Andersson (1967).
Taiga soils, Africa	14			25	Do.
Soils, European U.S.S.R.	130	40	5,000		Aidin'yan, Trofakh, and Balavchara (1964).
Soils, Donets Basin	548	<20	10,000	400	Dvornikov (1967).
Soils, Donets Basin		100	2,000	1,000	Dvornikov and Petrov (1967).
Soils, Kerch Peninsula	284	<100	1,000		Murenov (1967).
Soils, Kerch-Taman area		210	1,000		Karpuk and Murenov (1964).
Soils, Viet Nam		30	1,000	400	Aidin'yan, Trofakh, and Balavchara (1964).

TABLE 11.—*Mercury content of natural waters, in micrograms per liter*

(1 microgram per liter = 1 part per billion mercury)

Sample	Number of samples	Range		Average	Reference
		Min	Max		
Rivers					
Rhine River				0.1	Stock and Cucuel (1934a).
Saale River, Germany	6	0.02	0.10	.07	Heide and Weihe (1957), and Heide, Lotz, and Weihe (1957).
Elbe River, Germany	1			.00	Do.
Danube River		1	3		Aidin'yan and Batsevskaya (1983).
Sweden	1	.05	.2		Ackefors (1986).
European USSR	63	1	3.5	1.1	Aidin'yan (1982).
Armenian SSR	7	1	20	1.3	Aidin'yan (1983).
Armenian SSR	6		1.0	.1	Do.
	600	.01	1100	1.1	
Sea water					
				0.01	Stock and Cucuel (1934a).
				.04	Heide and Weihe (1957).
Atlantic, Indian, Red Sea, Black Sea, etc	14	0.1	1.0	1.1	Aidin'yan (1982).
Atlantic Ocean	6	.1	1.0	1.2	Aidin'yan, Gorbova, and Glaz (1981).
Pacific Ocean, Ramapo Deep		.08	.10	.1	Ramage-ichi and others (1981).
Do	4	.13	.17	.3	Hasebara (1981).
Minamata Bay, Japan		1.6	4.6		Hasebara and others (1981).
Ground water and miscellaneous samples					
Rain water		0.03	0.43	0.3	Stock and Cucuel (1934a).
Spring water, Germany		.01	.03		Do.
Surface waters, Northeast Caucasus	1,000	.01	.08		Baev (1986).
Subsurface waters, Northeast Caucasus	47	.01	1.25		Do.
Springs, Khoya region		.05	60	.1	Kratsov, Vidyev, and Kotel'kova (1988).
(No data in abstract on nature of water.)		0	140,000		Tabitura and Shidara (1988).
Ground water, Kerch, USSR		.1	.3		Morozov (1962).
Ground water, near mud volcanoes, Kerch		1	3.5		Karasik and Marinov (1966).
Ground water, Abkhazia, USSR				.5	Zautashvili (1966).
Mine waters, Abkhazia, USSR		.5	3		Do.
Mineralized waters, Abkhazia, USSR		1	7		Do.
Waters of Permian salt beds, Donets Basin	20	.1	6.5		Karasik, Goncharov, and Vasilevskaya (1967).
Brines associated with petroleum, Cymric oil-field, California		100	100		Bailey and others (1981).
Brine, geothermal well, Salton Sea, Calif	1			6	Skinner and others (1967).

[1] The value 0.13 (next highest value) is ascribed to waste water from an industrial plant.

[2] Excluding the highest value.

[3] Values from 0.1 ppb were in the 1 ppm area of mercury contamination.

TABLE 15.—*Mercury in air and in volcanic emanations, in nanograms per cubic meter*

[1 nanogram = 10⁻⁹ grams]

Sample	Number of analyses	Range		Average	Reference
		Min	Max		
Air					
"Unpolluted air"	8			5	Stock and Cucuel (1934b).
Over Pacific Ocean, 20 miles offshore		0.6	0.7		Williston (1968).
California, winter			62		Do.
California, summer			50		Do.
Background, Arizona and California		4	7.9	4.9	McCarthy and others (1969).
Chicago area	62	5	80	6.7	Dyer and others (1969).
Kamchatka	16			100	Aidinyan and Osetrova (1968).
Nevada and Yuta regions, no ore deposits:		60	300		Do.
Over porphyry copper deposit		12	70	18.6	McCarthy and others (1969).
Do.		15	53	28.4	Do.
Over mercury deposit		12	57.5	31.4	Do.
Do.		23	60	40	Do.
Do.		600	1,000		Karasik and Rul'shatov, quoted by Aidinyan and Osetrova (1968).
Volcanic					
Air of vent breccias of mud volcanoes		600	700		Karasik and Mirsaev (1968).
Gases of mud volcanoes		700	2,000		Do.
Gases, Mendeleev and Shiveluch Volcanoes		500	1,000		Aidinyan and Osetrova (1968).
Gases from hot springs, Kamchatka and Kuriles		10,000	17,000		Do.
Condensates from fumaroles and volcanic emanations, Kamchatka and Kuriles		1.2	12		Do.
Waters from hot springs, Kamchatka and Kuriles		1.5	4		Do.

[ppb, parts per billion]

TABLE 16.—*Mercury in coal, in parts per billion*

Sample	Number of samples analyzed	Range		Average	Reference
		Min	Max		
Germany	11	1	83	17	Stock and Cucuel (1934b).
Donets Basin, U.S.S.R.		4,000	70,000	11,000	Karasik and others (1963).
Do.		140	400,000	15,000	Osetrova (1967).
Do.	800	50	10,000	1,000	Dvornikov (1967).
Donets Basin, U.S.S.R. (in lenses within mercury ore body)		6,000	6,000	1,000	Rul'shatov (1967).
Donets Basin, U.S.S.R.	75	80	60,000		Dvornikov (1967a).
Do.		100	1,000		Dvornikov (1967b, 1967c).
Do.	13	100	400,000	40,000	Dvornikov (1968).

TABLE 15. *Mercury content, in parts per billion, of some sedimentary stratigraphic units in the Colorado Plateau region of the United States*

[Units are arranged in order of youngest (Tertiary) to oldest (Permian and Pennsylvanian)]

Stratigraphic unit	Number of samples	Mode	Highest	Lowest	Median (2 samples)	Dominant rock type	Approximate thickness (feet)
Tertiary: northern Colorado Plateau region							
Uinkaret Mesa Formation	60	60	180	15	47–100	Sandstone	1,500
Uinta and Green River Formations	200	100	1,000	15	43–100	Shale, sandstone	5,000
Wasatch and Fortin Formations	150	200	1,100	50	150–300	Shale, sandstone	2,000
Cretaceous: northern Colorado Plateau region							
Mesaverde Group and Mancos Shale	150	250	1,500	30	140–400	Mudstone, sandstone	5,000
Jurassic: Colorado Plateau region							
Morrison Formation	250	100	>10,000	10	84–150	Sandstone, mudstone	1,000
Entrada Sandstone	250	100	1,000	50	60–300	Sandstone	300
Carmel Formation	60	100	700	10	50–170	Sandstone, siltstone	300
Navajo Sandstone	61	40	500	<10	10–150	Sandstone	1,000
Triassic: Colorado Plateau region							
Wingate Sandstone	100	400	1,000	60	140–170	Sandstone	300
Chinle Formation	250	100	700	60	120–170	Sandstone, siltstone	1,000
Cutler Formation	150	100	>10,000	60	80–100	Mudstone, sandstone	1,000
Moenkopi Formation	121	170	>10,000	<10	80–120	Siltstone, sandstone	1,000
Upper Paleozoic: Colorado Plateau region							
Cutler Formation (Permian)	30	170	1,000	30	100–300	Sandstone, conglomerate	1,000
Hermosa Formation (Pennsylvanian) and Supai Formation (Permian and Pennsylvanian)	61	300	3,000	50	100–170	Limestone, siltstone	3,000

[Sampled only in east part of region] [Sampled only in central part of region]

TABLE 16. *Equilibrium constants and standard potentials at 25 C and 1 atmosphere pressure*

[E = [illegible]; K = [illegible]; log K = [illegible]]

Equation	log K	E° (volts)	Source of data
[illegible]		0.789	Latimer (1952)
[illegible]		.771	[illegible]
[illegible]		.533	[illegible]
[illegible]			[illegible]
[illegible]			Calculated from data in Wagman and others (1968)
[illegible]		.045	Latimer (1952)
[illegible]			[illegible]
[illegible]			Helgeson (1969)
[illegible]			[illegible]
[illegible]		.185	Latimer (1952)
[illegible]			Calculated from data in Wagman and others (1968)
[illegible]			Helgeson (1969)
[illegible]			[illegible]
[illegible]			Calculated from data in Wagman and others (1968)
[illegible]			[illegible]
[illegible]			[illegible]
[illegible]			Calculated from data in Latimer (1952) and Wagman and others (1968)
[illegible]			Calculated from data in Wagman and others (1968)
[illegible]			Calculated from data in Wagman and others (1968); Wagman and others (1968)
[illegible]			[illegible]
[illegible]			[illegible]
[illegible]			[illegible]

TABLE 60.—*Standard free energies of formation of certain mercury species, in kilocalories per mole*

[Leaders indicate no common name. Le Chatelier, H., 1888, C. R. Acad. Sci. [Paris], 106, [number] species]

Formula	Description	Free energies (kcal)
Hg	Metallic mercury	0
Hg	Mercury vapor	15
Hg	Dissolved mercury	0
Hg	Mercurous ion	37
Hg	Mercuric ion	39
Hg_2Cl_2	Calomel	50
$HgCl_2$	Mercuric chloride	42
HgO	Red oxide	13
HgO	Yellow oxide	13
HgS		12
HgS		12
HgS		6
HgS	Cinnabar	12
HgS	Metacinnabar	12
$HgSO_4$		140
$HgCO_3$		105
$HgCl_2$		44
HgCl		50

TABLE 61.—*Mercury concentrations from results of analyses of selected thermal and mineral waters and their deposits, Northern California mercury district*

(Detection limit, 0.01 part per billion. N.d., not detected. Analyses by M. E. Hinkle)

Sample	Remarks	Mercury concentration (ppb)
Condensates, condensate soil marked in ice		
McLaughlin well 1	Lake	1.8
McLaughlin well 5	do.	
Waters of low to moderate salinity, 1–10 ‰		
Allen Spring	Lake	2.1
Harriet Spring	do.	2.1
Spring east of Alice mine	Colusa	2.1
Waters of high salinity, 1–10 ‰		
Grizzly Spring	Lake	2.1
Abbott Mine water	do.	2.1
Dead Shot Spring	Colusa	2.1
Wilbur oil test well	do.	0.7
Salt spring north of Wilbur Springs	do.	1
Complexion Spring	Lake	4
Salt Spring north of Stonyford	Colusa	2.1
Redbrae Spring (Foutz Springs)	Colusa	2.1
Waters of low salinity, 1–10 ‰		
Castle Rock Spring	Lake	2.1
Anderson Spring	do.	2.1
Seigler Spring	do.	2.1
Waters of moderate to high salinity, 1–10 ‰		
Sulphur Bank	Lake	1.8
Wilbur Springs	Colusa	1.8
Solids		
Sulfur floating on Wilbur Springs	Colusa	10,000
Magnesia-silica gel from Complexion Spring	Lake	500
Silica-magnesia gel from Aqua de Ney	Siskiyou	500

TABLE 32.—*Mercury concentrations in thermal waters from Yellowstone National Park*
(Detection limit, 0.01 part per billion. N.d., not detected. Analyses by M. E. Hinkle)

Sample	Location	Mercury concentration (in ppb)
Ole Caliente	Midway Basin	0.14
Hot Spring	do	.07
Rabbit Spring	do	.07
Chinaman Spring	do	.16
Steady Geyser	Lower Basin	.07
Small Spring	Porcupine Hills	.10
Pearl Spring	Gibbon Canyon	.12
Little Whitefish Spring	Norris Basin	.07
Cinder Pool	do	.08
Spring, base of Porcelain Terrace	do	.16
Echinus Geyser	do	.17
Cistern Spring	do	.08
Primrose Spring	Sylvan Spring area	.13
Sulfur Pool	do	.15
Green Spring	do	.10
Blue Spring	do	.10
New Highland Terrace	Mammoth Spring	.01

TABLE 33.—*Mercury concentrations from analyses of petroleum from the Wilbur Springs area, northern California*
(Detection limit, 0.01 part per billion. Analyses by M. E. Hinkle)

Sample	County	Mercury concentration (in ppb)
Lurgi petroleum, Abbott mine	Lake	500–1000
Petroleum, Wilbur oil test well	Colusa	1–500

TABLE 34.—*Mercury in selected rivers of the United States, 1970*
(Analyses by M. J. Fishman, U.S. Geological Survey, written commun., 1970)

Name and location	Time sample collected		Mercury (in ppb)
	Month-day	Hour	
Gold Creek at Juneau, Alaska	8-10	1430	0.1
Colorado River near Yuma, Ariz.	8-18		.1
Wellton-Mohawk Drain near Yuma, Ariz.	8-18		.1
Dewitts Bluff near Yuma, Ariz.	8-18	0900	.1
Ouachita River downstream from Camden, Ark.	8-18	1000	.1
St. Francis River at Marked Tree, Ark.	8-20		.1
Santa Ana River below Prado Dam near Riverside, Calif.	8-19	1410	.1
South Platte River at Henderson, Colo.	8-18		.1
Blue River upstream of Dillon Reservoir, Colo.	8-18		.1
Vasquez Creek near Breckenridge, Colo.	8-18		.1
Animas River at Durango, Colo.	8-18		.1
Cement Creek at Silverton, Colo.	8-18		.1
Red Mountain Creek near Ouray, Colo.	8-18		.1
Red Mountain Creek at Ironton, Colo.	8-18		.1
Manoa Stream near Honolulu, Hawaii	8-6	0930	.0
Waiakeawaena Stream near Papaikou, Hawaii	8-6	1015	.1
North Fork Kaukonahua near Wahiawa, Hawaii	8-11	1030	.1
Ohio River near Grand Chain, Ill.	8-26	1040	.2
Floyd River at Sioux City, Iowa	8-6	1045	.0
Kansas River downstream from Topeka, Kans.	8-10	1100	.1
Mississippi River near Hickman, Ky.	8-25	1030	.1
Merrimack River above Lowell, Mass.	8-6	1100	.1
Wolf Creek near Cedar Lake, Mich.	8-7	1400	.1
Tributary to Wolf Creek near Edmore, Mich.	8-7	1000	.1

TABLE 24.—*Mercury in selected rivers of the United States, 1970.*—Continued

[Analyses by M. T. Brown, U.S. Geological Survey, unless otherwise noted. 1970]

River and location	Time sample collected		Mercury in ppb
	Month-day	Hour	
Rainy River at International Falls, Minn	8-17	1012	0.1
St. Louis River at Scanlon, Minn	8-17	1015	0.1
Pearl River at Byram, Miss	7-15	1100	0.4
Pascagoula River at Merrill, Miss	7-15	1100	0.4
Yellowstone River near Billings, Mont	8-14	1700	0.1
Missouri River near Great Falls, Mont	8-14	1700	0.1
Missouri River near St. Louis, Mo	8-21	1030	0.2
Missouri River at Hermann, Mo	8-21	1030	0.2
Salt Creek near Lincoln, Nebr	6-24	0915	.5
Las Vegas Wash at Henderson, Nev	5-14		0.1
Pemigewasset River at Woodstock, N.H	8-6	1700	0.1
Canadian River near Ilfeld, N. Mex	8-18	1100	0.1
Hudson River downstream from Poughkeepsie, N.Y	7-7		0.1
Creek River near Scotia (Central Vt. to Rutland and Essex County), N.Y	7-21	1215	0.1
Wappinger Creek near Wappingers Falls, N.Y	7-21	1230	0.1
Delaware River at Port Jervis, N.Y	7-21	1330	0.1
Beaver Kill at Cooks Falls, N.Y	7-21	0945	0.1
Bear River near Delevan, N.Y	7-21	0915	0.2
Tonawanda Creek at Batavia, N.Y	7-21	0900	0.2
Genesee River at Mount Morris, N.Y	7-21	0900	0.2
Oswego River at Phoenix, N.Y	6-16	1000	.1
Black River at Watertown, N.Y	7-8	1015	0.1
Black River near Watertown, N.Y			0.1
Lake Champlain near Willsboro, N.Y			0.1
Lake Champlain near Peasleeburg, N.Y			0.1
Lake Champlain near Chazy, Point, N.Y			0.1
Hudson River at Waterford, N.Y	8-18	0930	0.1
Hudson River at Poughkeepsie, N.Y	8-18	0930	0.1
Hudson River at Catskill, N.Y	8-18	1130	0.1
Oswegatchie River at Heuvelton (Trib. to Lawrence County), N.Y	8-18	1130	0.1
Oswegatchie River at Rensselaer, N.Y	7-8	1015	0.1
Chemung River near Waverly, N.Y	7-8	1030	0.1
Susquehanna River at Johnson City, N.Y	7-8	1030	0.1
Maumee River at Antwerp, Ohio	8-19	1215	0.2
Scioto River near Circleville, Ohio	8-17	1215	0.2
Great Miami River near Miamisburg, Ohio	8-17	1215	0.2
North Canadian River near Harrah, Okla	8-18	1000	0.1
North Canadian River near Bethany (Okla. City), Okla	8-18	1000	0.1
Whitewood Creek near Vale, S. Dak	7-22	1100	0.1
Paint Mill Creek near Hurst, Tex	8-11	1700	0.1
San Antonio River near Elmendorf, Tex	8-11	1700	0.1
Blackwater River at Franklin, Va	8-13	0930	0.1
Jackson River near Covington, Va	8-13	0930	0.1
Mossy Creek near Hopewell, Va	8-13	0930	0.1
Snohomish River near Monroe, Wash	7-1	1030	0.1
North Branch Potomac River near Bayard, W. Va	8-1	1000	0.1
Wisconsin River at Wisconsin Dells, Wis	8-18	1700	0.2
Wisconsin River near Necedah, Wis	8-18	1700	0.2
North Platte River near Lyman, Wyo	8-10	1015	0.1
Bighorn River at Kane, Wyo	8-10	1000	0.1

TABLE 65.—*Mercury levels in natural waters outside the United States*

Location	Concentration (ppb)	Reference
Sea water, vicinity of Helgoland	0.03	Stock and Cucuel (1934).
Jamaica Deep	0.0 0.2	Hamaguchi and others (1961).
Kuroshio Deep (Pacific Ocean, southeast of Honshu, Japan)	.15 .37	Hamahara (1961).
Minamata Bay, Japan	1.0 6.0	Omohara and others (1961).
Sea waters of U.S.S.R.	0.1	Sidko'van (1962).
Volga, Ural, Arakes, and Dnepr's Rivers	0.1	Sidko'van and Belyavskaya (1964).
Rivers of European U.S.S.R.	0.1	Sidko'van (1962).
Armenian rivers and Sevan Lake (Armenia)	0.1	Sidko'van (1962).
Rivers near the mercury deposits of Abkhazia, U.S.S.R.	0.1	Pantsakvelli (1960).
Natural waters of Germany	.01 .9	Stock and Cucuel (1934).
Saale River, Germany	0.15 1.0 (avg. .067)	Heide, Lenz, and Hobel (1937).
Uncontaminated river waters of Italy	.01 .07	Dall'Aglio (1962).
Rivers near mercury deposits of Italy	Up to 1.00	Do.

TABLE 66.—*Mercury consumption, in kilograms, in the United States for calendar year 1969 and the first quarter of calendar year 1970*

(Source: Mineral Industry Surveys, U.S. Bureau of Mines, first quarter, 1970)

Use	1969				1st quarter, 1970			
	Primary	Redistilled	Secondary	Total	Primary	Redistilled	Secondary	Total
Agriculture	91,100			91,100	20,000			20,000
Amalgamation	3,600	45		3,645	1,000	455		1,455
Catalytic preparations	1,000	1,000	10,000	12,000	1,000	455	1,000	2,455
Electrical apparatus	1,000	1,000	10,000	12,000	1,000	455	1,000	2,455
Electrolytic preparation of chlorine and caustic soda	45,000	1,000	10,000	56,000	10,000	455	1,000	11,455
General laboratory and control instruments	10,000	1,000	2,000	13,000	2,000	455	1,000	3,455
Paints								
Pharmaceuticals	2,000	45		2,045	1,000	455		1,455
Primary metallurgy	2,000	45		2,045	1,000	455		1,455
Other uses	10,000	1,000	1,000	12,000	2,000	1,000	1,000	4,000
Total consumption	3,000	1,000	10,000	14,000	1,000	1,000	1,000	3,000
Grand total	3,000,000	100,000	100,000	3,200,000	500,000	50,000	50,000	600,000

[Withheld figures are included in appropriate totals]

TABLE 27. *Lethal concentrations of mercury compounds for various aquatic organisms and man*
[Data summarized from sources published in part]

Organism	Lethal concentration (ppm)	Mercury compound
Aquatic organisms		
Bacteria:		
Escherichia coli	1000	Mercuric chloride.
	1000	Mercuric cyanide.
	1000	Ethylmercuric bromide.
	1000	Phenylmercuric chloride.
	1000	Ethylmercuric oxalate.
Phytoplankton:		
Marine diatoms	60	Ethyl mercury phosphate.
Nitzschia closterium	100	Mercuric chloride.
	1.0	Mercuric cyanide.
Protozoa:		
Tetrahymena	1.00	Mercuric chloride.
	1.00	Mercuric cyanide.
Zooplankton:		
Daphnia pulex	.5	Phenylmercuric acetate.
Daphnia magna	.01	Mercuric cyanide.
	.6	Mercuric chloride.
Amphipod:		
Marinogammarus marinus	100	Mercuric chloride.
Isopod:		
Mesosphaeroma oregonensis	15	Mercuric nitrate.
Flatworm:		
Polycelis nigra	270	Mercuric chloride.
Polychaete:		
Nereicirella conjunctiva	1,000	Mercuric nitrate.
Mollusca:		
Oyster larvae	97	Mercuric chloride.
Australorbis glabratus	1,000	Do.
Fish:		
Stickleback	100	Mercuric nitrate.
	1.0	Mercuric chloride.
Guppy	100	Mercuric nitrate.
	100	Mercuric chloride.
Shiner	600	Ethyl mercury phosphate.
Pike	27	Mercuric chloride.
Channel catfish	200	Phenylmercuric acetate.
Rainbow trout	1,000	Ethyl mercury phosphate.
	1,000	Methylmercuric acetate.
Salmon	100	Mercuric chloride.
	10	Phenylmercuric acetate.
	10	Mercuric acetate.
Man		
Adult, death	1.9	Mercuric chloride.
Adult, chronic illness	1.7	Do.

[1] Oral.

TABLE 28.—*Maximum mercury concentration in air measured at scattered mineralized and non-mineralized areas of the Western United States*

[... no data available]

Sample location	Maximum Hg concentration (ng/m³)	
	Volatile	Total Hg
Mercury mines		
[illegible]	[illegible]	[illegible]
Base and precious metal mines		
[illegible]	[illegible]	[illegible]
Porphyry copper mines		
[illegible]	[illegible]	[illegible]
Unmineralized areas		
[illegible]	[illegible]	[illegible]

[illegible]